PHORATE (112)

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EXPLANATION

Residue and analytical aspects of phorate were evaluated by the JMPR in 1977, 1984, 1990, 1991, and 1992. The compound has been included in the JMPR periodic review programme and is scheduled for residues evaluation in 2005. The toxicological review was conducted in 2004, which established an ADI of 0–0.0007 mg/kg bw and an ARfD of 0–0.003 mg/kg bw.

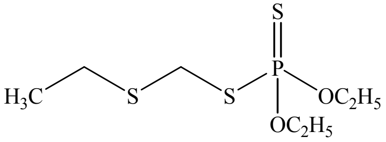
Since its last residues evaluation by JMPR, phorate has undergone a number of reviews by national governments for purposes of re-registration. These reviews included those conducted by the US EPA and Canada's PMRA. As a result of these national reviews, the approved uses and labels have been amended.

Information on the latest GAP, residue data, metabolism, analytical methods, storage stability and processing studies are provided to enable the assessment of existing and proposed MRLs on a number of crops or crop groups, including beans, potatoes, sugarbeets, sweet corn, maize, sorghum, cotton, and coffee.

In addition, GAP information and/or national MRLs were supplied by Australia and The Netherlands.

IDENTITY

ISO common name:	phorate
Chemical name	
IUPAC:	O,O-diethyl-S-ethylthiomethyl phosphorodithioate
CA:	O,O-diethyl-S-[(ethylthio)methyl]phosphorodithioate
CAS Registry No:	298-02-2
CIPAC No:	-
Synonyms and trade names:	O,O-diethyl S-[(ethylthio)methyl]ester of phosphorodithioic acid; phosphorodithioic acid, O,O-diethyl S-(ethylthio)methylester; O,O-diethyl S-ethylmercaptomethyl phosphorodithioate. Thimet; Timet (USSR); CL 35,024; EI 3911; AC 3911; ENT 24042
Structural formula:	confirmation spectra not submitted



Molecular formula:	$C_7H_{17}O_2PS_3$
Molecular weight:	260.4

Physical and Chemical Properties

Pure active ingredient

Most experiments were carried out with the technical material (> 90% purity).

Parameter	Result	References	Guidelines
Minimum purity:	not indicated	-	-

Parameter	Result	References	Guidelines
Appearance:	Colourless to pale yellow liquid with a mercaptan-like odour (technical material)	Luckhowec, 1989 [PA-140-002]	EPA 63-2 to 63-4
Vapour pressure:	85.8 mPa (6.44 x 10^{-4} mm Hg) at 25 °C 171 mPa (12.8 x 10^{-4} mm Hg) at 35 °C 273 mPa (20.5 x 10^{-4} mm Hg) at 45 °C gas saturation technique (analytical standard, purity not stated)	Luckhowec, 1989 [PA-140-002]	EPA 63-9
Melting/freezing point:	not required (liquid at room temperature)	Luckhowec, 1989 [PA-140-002]	EPA 63-5
Octanol/water partition coefficient:	log K_{ow} = 3.92 at unstated pH and 25 °C for 4.8 and 0.53 mg/L in water after equilibrium (purity 98.6%)	Luckhowec, 1989 [PA-140-002]	EPA 63-11
Solubility:	29 mg/L in water at 25 °C flask method (purity 99.1%)	Luckhowec, 1989 [PA-140-002]	EPA 63-8
	>1000 g/L at 20°C for each of following: acetone, ACN, n-heptane, DCM, and toluene (purity 91.3%).	Luckhowec, 1989 [PA-140-002]	EPA 63-8
Relative density:	1.16 g/cm^3 at 20 °C (purity 91.3%)	Luckhowec, 1989 [PA-140-002]	EPA 63-7
Hydrolysis:	DT_{50} = 2.36 d at pH 5 and 25 °C DT_{50} = 2.47 d at pH 7 and 25 °C DT_{50} = 2.08 d at pH 9 and 25 °C	Martin and Heim, 1999 [PA-630-005]	
Photolysis:	no data submitted	-	-
Dissociation constant:	not applicable, active ingredient does not dissociate	Luckhowec, 1989 [PA-140-002]	EPA 63-10

Technical material

Parameter	Result	References	Guidelines
Minimum purity	90%	Tomlin, 2000	-
Main impurities:	no data submitted	-	-
Appearance:	Colourless to pale yellow liquid with a mercaptan-like odour (technical material)	Luckhowec, 1989 [PA-140-002]	EPA 63-2 to 63-4
Relative density:	1.16 g/cm^3 at 20 °C wide-mouth pycnometer (volumetric flask) method (purity 91.3%)	Luckhowec, 1989 [PA-140-002]	EPA 63-7
Melting range:	not required (liquid at room temperature)	Luckhowec, 1989 [PA-140-002]	EPA 63-5
Stability:	Study 1 99.1% recovery after 3 months at 45 °C 97.3% recovery after 12 months at 37 °C 99.2% recovery after 24 months at room temperature (purity 88.5%)	Luckhowec, 1989 [PA-140-002]	EPA 63-13
	Study 2 The material showed a decomposition exotherm starting at 172 °C (differential thermal analysis) (technical material)	Luckhowec, 1989 [PA-140-002]	EPA 63-13
	Study 3 100% recovery after being in contact with 304 stainless steel, 316 stainless steel, C1020 carbon steel and AL3003 aluminium for 4 weeks at 54 °C (purity 92.1%)	Luckhowec, 1989 [PA-140-002]	EPA 63-13
	Study 4 100% recovery after storage in the original packaging material for 14 months at room temperature (purity 92.1%)	Luckhowec, 1989 [PA-140-002]	EPA 63-17

Formulations

Phorate is available in granular formulations with active ingredient content of 5%, 10%, 15%, or 20%. FAO specifications for technical and formulated phorate are not available.

Codes used in study reports for active ingredient and metabolites

Code	Name and synonyms	Found in:
CL 35,024	phorate	goat, h-; plants; soil, water
CL 18,177	phorate sulfoxide; phosphorodithioate sulfoxide phosphorodithioic acid, S-[(ethylsulfinyl)methyl] O,O-diethyl ester; phosphorodithioic acid, O,O-diethyl S-(ethylsulfinyl)methyl ester; O,O-diethyl S-[(ethylsulfinyl)methyl] phosphorodithioate O,O-diethyl S-ethylsulfinylmethylphosphorodithioate	goat, h-; plants; soil, water
CL 18,161	phorate sulfone; phosphorodithioate sulfone phosphorodithioic acid, S-[(ethylsulfonyl)methyl] O,O-diethyl ester; phosphorodithioic acid, O,O-diethyl S-(ethylsulfonyl)methyl ester; O,O-diethyl S-[(ethylsulfonyl)methyl] phosphorodithioate; O,O-diethyl S-ethylsulfonylmethylphosphorodithioate	goat, h-; plants; soil
CL 4,259	phoratoxon; phorate oxygen analogue; phosphorothioic acid, O,O-diethyl S-(ethylthio)methyl ester; O,O-diethyl S-[(ethylthio)methyl] phosphorothioate; O,O-diethyl S-ethylthiomethylphosphorothiolate	goat, h-; plants; soil
CL 18,162	phoratoxon sulfoxide; phorate oxygen analogue sulfoxide; phosphorothiolate sulfoxide; phosphorothioic acid, O,O-diethyl S-(ethylsulfinyl)methyl ester; O,O-diethyl S-[(ethysulfinyl)methyl] phosphorothioate; O,O-diethyl S-ethysulfinylmethylphosphorothiolate	goat, h-; plants; soil
CL 18,061	phoratoxon sulfone; phorate oxygen analogue sulfone; phosphorothiolate sulfone phosphorothioic acid, O,O-diethyl S-(ethylsulfonyl)methyl ester; O,O-diethyl S-[(ethylsulfonyl)methyl] phosphorothioate; O,O-diethyl S-ethylsulfonylmethylphosphorothiolate;	goat, h-; plants; soil
CL 1008536	des-ethyl phorate sulfoxide; phosphorodithioic acid, S-[(ethylsulfinyl)methyl] O-ethyl ester;	-
CL 1008535	des-ethyl phorate sulfone; phosphorodithioic acid, S-[(ethylsulfonyl)methyl] O-ethyl ester	-
CL 180,296	ethylsulfonyl methylsulfonyl methane	goat, hen plants soil
CL 180,297	(ethylsulfinyl) methyl methyl sulfone; ethyl (methylsulfonyl)methyl sulfoxide	goat, hen
CL 180,298	ethyl (methylsulfinyl)methyl sulfone (ethylsulfonyl)methyl methyl sulfoxide	goat, hen
CL 325,959	(ethylsulfinyl)(methylsulfinyl) methane	hen
-	phosphoric acid	plants
-	O,O-diethyl phosphoric acid	plants
-	O,O-diethyl phosphorothioic acid	plants
-	O,O-diethyl phosphorodithioic acid	plants
-	formaldehyde	water

h- not found in laying hens, p- not found in plant; s- not found in soil

METABOLISM AND ENVIRONMENTAL FATE

Animal metabolism

The Meeting received information on the fate of orally dosed phorate in lactating goats and laying hens. Phorate was ^{14}C labelled at the methylene position as indicated in figure 1. Metabolism in laboratory animals (rats) was summarized and evaluated by the WHO panel of JMPR in 2004.

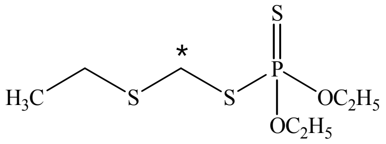


Figure 1. Label position in ^{14}C labelled phorate used in metabolism studies

Lactating goats

Study 1. In a preliminary dose-titration study two lactating goats were administered unlabeled phorate once daily by capsule for three consecutive days (Hussain, 1985, PA-440-003 and Miller, 1986, PA-440-008). Average weight of the goats was 42 kg; breed and age were not stated. In phase A the goats received 1.35 or 2.70 mg ai/kg feed, equivalent to 1× and 2× treatment. In phase B the same goats received 4.05 or 5.40 mg ai/kg feed, equivalent to 3× and 4× treatment; phase B was not started until the plasma acetylcholinesterase values after the first treatment were back to normal. Significant depression in plasma acetylcholinesterase activity was observed at the 4× treatment, although no significant decrease in milk production was noted. Consequently the 4× treatment level was chosen as highest dose in the metabolism study.

In the metabolism study, 14C-phorate was administered daily in gelatin capsules for 7 consecutive days to two lactating goats, while one control goat received placebos. Goats had an average weight of 47.3 kg (range 43.0-55.0 kg); breed and age were not stated. Capsules were administered by balling gun. Dosages were equivalent to 0 (control), 1.35 mg ai/kg (1×), and 5.40 mg ai/kg (4×) in the feed, assuming an average daily feed intake of 2.9 kg. Actual dose rates in mg ai/kg feed or mg ai/kg bw were not stated. Phorate was 14C labelled at the CH_2 group located between the two sulfur atoms. The radiopurity was > 98%, the specific activity 40 µCi/mg for the undiluted radiolabel, and 1.1 µCi/mg for the administered radiolabel. Milk samples were collected daily up to the time of sacrifice. Morning milk samples were pooled with milk samples taken in the afternoon just prior to dosing. Goat 181 (control) and goat 180 (1x treatment) were sacrificed 16 hrs after last dosing, goat 178 (4× treatment) was found asphyxiated in its yoke in the 16-hr interval between the last dose and the scheduled time of sacrifice. Omental fat, leg muscle, tenderloin muscle, kidney, and liver were collected. Milk was kept refrigerated and tissue samples were kept frozen until analysis. Storage time and temperature were not stated.

Total ^{14}C-radioactivity was determined by (combustion) LSC. The LOQ was 0.05 mg/kg eq for tissues and 0.01 mg/kg eq for milk. Total radioactive residues (TRRs) in milk were < 0.01 mg/kg eq in the control goat, 0.04 to 0.11 mg/kg eq for the 1x treatment and 0.20 to 0.50 mg/kg eq for the 4x treatment. Residue levels in milk increased steadily and no plateau was reached during the dosing period. Liver, kidney, leg muscle, tenderloin muscle and fat tissue samples showed TRRs of < 0.05 mg/kg eq for the control goat, 0.23, 0.14, 0.13, 0.07 and < 0.05 mg/kg eq respectively at the 1x treatment level and 0.90, 0.76, 0.96, 0.31, and 0.21 mg/kg eq respectively at the 4× treatment level. Recovery of total applied radioactivity (in excreta, tissues, milk) was not investigated, and residues were not characterized.

Study 2. 14C-phorate was administered daily in gelatin in capsules for 3 consecutive days to two lactating goats with an average weight of 50 kg (Hussain, 1986, PA-440-004 and PA-440-005 and Miller, 1986, PA-440-008). Breed and age were not stated. The goats used, were the same goats as used for the preliminary study in study 1. Capsules were administered by balling gun. Dosages were equivalent to 5.40 mg ai/kg (4×) in the feed, assuming an average daily feed intake of 2.9 kg. Actual dose rates in mg ai/kg feed or mg ai/kg bw were not stated. Phorate was ^{14}C labelled at the CH_2 group located between the two sulfur atoms. The radiopurity was > 98%, the specific activity 40 µCi/mg for the undiluted radiolabel, and 17.1 µCi/mg for the administered radiolabel. Milk samples were collected daily up to the time of sacrifice. Morning milk samples were pooled with milk samples taken in the afternoon just prior to dosing. Goats were sacrificed 16 hrs after last dosing. Omental fat, leg muscle, tenderloin muscle, kidney, and liver were collected. Milk was kept refrigerated and tissue samples were kept frozen until analysis. Storage time and temperature were not stated.

Total ^{14}C-radioactivity was determined by (combustion) LSC. The LOQ was 0.05 mg/kg eq for tissues and 0.01 mg/kg eq for milk. Total radioactive residues (TRRs) in milk ranged from 0.20 to 0.30 mg/kg eq for goat 176 and 0.20 to 0.31 mg/kg eq for goat 179. Residue levels in milk increased steadily and no plateau was reached during the dosing period. Liver, kidney, leg muscle, tenderloin muscle and fat tissue samples showed TRRs of 0.67, 0.46, 0.22, 0.19 and < 0.05 mg/kg eq respectively for goat 176 and 0.58, 0.37, 0.18, 0.16, and < 0.05 mg/kg eq respectively for goat 179. Residue levels in pooled milk and pooled tissues as used for metabolite profiling are shown in table 1. Recovery of total applied radioactivity (in excreta, tissues, milk) was not investigated.

Composite milk samples from days 1 to 3 were extracted with EtOH, followed by centrifugation to precipitate proteins. The EtOH-milk solution was concentrated by evaporation under vacuum. Tissue samples were extracted with a mixture of MeOH/ACN; tissue extracts from both goats were combined. Extracts were analysed by one dimensional TLC with three subsequent solvent systems. All radioactive bands were removed and each band was analysed by three dimensional TLC (plates turned three times with three different solvent systems). Identification of the radioactive metabolites was by demonstration of exact co-chromatography with either radiolabelled metabolites isolated from a rat metabolism study (ethylsulfonyl methylsulfonyl methane; (ethylsulfinyl) methyl methyl sulfone; ethyl (methylsulfinyl)methyl sulfone, Hussain, 1985, PD-M 22-31:1-132) or non-radiolabelled synthetic reference compounds (parent, phorate sulfone, phorate sulfoxide, phoratoxon, phoratoxon sulfone, phoratoxon sulfoxide).

Metabolite profiles are shown in table 1. Extractability was essential 100% for EtOH extracts of milk and MeOH/ACN extracts of tissues. Approximately 95% to 99% TRR in extracts of milk, liver, kidney, leg muscle, tenderloin muscle, and omental fat was composed of non-phosphorylated metabolites, which result from cleavage of the phosphorus bond and the methylation of the resultant mercaptan. The major metabolite in all tissues and milk was ethylsulfonyl methylsulfonyl methane accounting for 94% to 99% TRR in the tissues and milk. This metabolite was isolated from rat urine; the structure was confirmed by mass spectrometry. The remaining radioactivity was composed of the parent compound and its various oxidative products (< 0.01% to 2.2% TRR).

Table 1. Metabolic profile in extracts of various tissues of goats treated with ^{14}C-phorate.

Metabolite	Milk	Liver	Kidney	Leg muscle	Tenderloin muscle	Omental fat
TRR (mg/kg eq)	0.26	0.62	0.41	0.20	0.18	0.04
ethylsulfonyl methylsulfonyl methane (%TRR)	94%	97%	95%	96%	97%	100%
(ethylsulfinyl) methyl methyl sulfone (%TRR	0.8%	< 0.01%	< 0.01%	2.0%	0.55%	< 0.01%
ethyl (methylsulfinyl)methyl sulfone (%TRR)	4.7%	< 0.01%	< 0.01%	0.8%	1.3%	< 0.01%
parent (%TRR)	0.02%	0.7%	< 0.01%	< 0.01%	0.01%	< 0.01%
phorate sulfone (%TRR)	< 0.01%	< 0.01%	< 0.01%	0.05%	0.03%	< 0.01%
phorate sulfoxide (%TRR)	0.15%	< 0.01%	0.61%	0.1%	0.04%	< 0.01%
phoratoxon (%TRR)	0.01%	0.1%	0.01%	0.1%	0.3%	< 0.01%
phoratoxon sulfoxide (%TRR)	< 0.01%	< 0.01%	1.1%	0.2%	0.08%	< 0.01%
phoratoxon sulfone (%TRR)	< 0.01%	0.7%	0.88%	0.4%	0.4%	< 0.01%
unknown (%TRR)	-	1.5%	2.2%	0.5%	1.2%	0.4%
Total	100%	100%	100%	100%	100%	100%

Laying hens

Five groups of white Leghorn laying hens were dosed via gelatin capsules for five consecutive days with ^{14}C-phorate (Miller, 1991, PA-440-006). Three groups of five hens each were dosed with 0 (group A), 1 mg ai/kg (group B, 10×) and 3 mg ai/kg (group C, 30×) in the feed with a specific activity of 4.1 µCi/mg for the administered radiolabel. Two groups (D and E) of 10 hens each were administered 3 mg ai/kg in the feed with specific activity of 19 µCi/mg for the administered radiolabel (containing a 1:1 ratio of ^{14}C- and ^{13}C- phorate). Phorate was ^{14}C labelled at the CH_2 group located between the two sulfur atoms, and purity was > 97%. Dosages were calculated, assuming an average daily feed intake of 124 g/hen for group A, C, D, E and 84 g/hen for group B. Actual dose rates were 0.93 - 3.67 - 3.03 - 3.17 mg ai/kg feed for group B, C, D, E, respectively. Dosage as mg ai/kg bw was not stated. Average bodyweight of the hens per group ranged from 1.395-1.508 kg; age was not stated. Eggs were collected daily and eggs were separated into whites and yolks. Excreta were collected daily. A 5 day composite sample for each bird was prepared and frozen. Hens were sacrificed 18 hours after the last dose with liver, kidneys, breast muscle and skin with adhering fat collected for total radioactive analyses. Samples were stored frozen, temperature and duration was not stated.

Radioactive residues were analysed by combustion LSC. Recoveries of the administered doses averaged 64% in Group B and 66% in Group C: 62–64% TAR in excreta, 0.7%–1.5% in eggs, 0.5%–0.8% in organs and 1.2% in carcass. Fortification of control excreta with ^{14}C-phorate resulted in a recovery of 78% after 24 hrs at room temperature. According to the study author, these results suggest that the low, but consistent overall recovery may be associated with the volatility of phorate and/or the low molecular weight of the metabolic products.

TRR in tissues and eggs is summarized in Table 2. Residue levels in egg yolks and whites increased steadily and no plateau was reached during the dosing period. Animals from group A (control) and E (3 mg ai/kg feed) were not analysed.

Group D tissues were used for metabolite identification. A modified Bligh-Dyer extraction procedure with MeOH/water chloroform (11:5:5) was used to fractionate liver and kidney. The chloroform layer was further partitioned with ACN and hexane. The skin/fat sample was extracted with hexane/MeOH. Eggs were extracted with ACN/hexane. The ACN layer was further extracted with EtOAc. Muscle was not extracted, since the total residue level was below 0.05 mg/kg eq. Post extracted solids from all tissues and eggs were treated with protease, followed by a sequential extraction with EtOAc and MeOH. Extracts were cleaned up by various techniques and analysed by 2D-TLC. Metabolites were co-chromatographed with known standards (parent, phorate sulfone, phorate sulfoxide, phoratoxon, phoratoxon sulfone, phoratoxon sulfoxide, ethylsulfonyl methylsulfonyl methane; (ethylsulfinyl) methyl methyl sulfone; ethyl (methylsulfinyl)methyl sulfone) and one radioactive metabolite of confirmed structure (methane, (ethylsulfinyl)(methylsulfinyl)) that had been isolated from a rat metabolism study.

The distribution and nature of the residues in tissues and eggs are summarised in Tables 3 and 4. Metabolites found in the tissues and eggs include ethylsulfonyl methylsulfonyl methane; (ethylsulfinyl) methyl methyl sulfone; ethyl (methylsulfinyl)methyl sulfone). One additional non-phosphorylated metabolite, methane, (ethylsulfinyl)(methylsulfinyl) was also found in the egg white. Neither the parent compound phorate, nor any of the oxidative metabolites phorate sulfoxide, phorate sulfone, phoratoxon, phoratoxon sulfoxide or phoratoxon sulfone was found in tissues or in eggs.

A portion of the hexane soluble radioactivity was converted to polar water-soluble residues after saponification. The study author indicates this fraction to be associated with lipids. Significant fractions of the radioactive residues in tissues and eggs were unextractable but were released by enzyme hydrolysis with protease. Since the released activity was highly polar and water soluble, it was concluded not to result from any of the phorate oxidative metabolites. The study author suggests that the radiocarbon was most likely incorporated into natural products in the tissues and eggs through a metabolic route such as the TCA cycle.

Table 2. Total radioactive residues in tissues and eggs of laying hens.

Group	liver (mg/kg eq)	kidney (mg/kg eq)	breast muscle (mg/kg eq)	skin/fat (mg/kg eq)	egg white (mg/kg eq) d 1-5	egg yolk (mg/kg eq) d 1-5
B, 1 mg ai/kg feed	0.05	< 0.05	< 0.05	< 0.05	< 0.05	< 0.05-0.05
C, 3 mg ai/kg feed	0.32	0.24	< 0.05	< 0.05	< 0.05-0.08	< 0.05-0.19
D, 3 mg ai/kg feed	0.30	0.23	0.031	0.047	0.048-0.10	0.017-0.20

Table 3. Distribution of ^{14}C-residues in extracts of tissues and eggs of laying hens (group D).

	Liver (%TRR)	Kidney (%TRR)	skin/fat (%TRR)	egg white #1 (%TRR)	egg white #2 (%TRR)	egg yolk (%TRR)
ACN	5.8	11	na	na	na	na
- EtOAc	na	na	na	22	23	9.9
- water	na	na	na	26	22	2.5
hexane	5.0	3.0	7.9	0.81	0	37
MeOH/water	30	39	37	na	na	na
PES: EtOAc	0	0	0	0	-	-
PES: MeOH	19	13	14	28	-	-
PES: water	27	26	23	20	-	49
PES-2	14	8.0	18	2.0	55	1.8
Total	100	100	100	100	100	100

na = not applicable, - not done

Table 4. Distribution and nature of the ^{14}C-residues in the tissues and eggs of laying hens (group D).

Metabolite/extract	Liver		Kidney		Skin/fat		Egg white (d-5)		Egg yolk (d-5)	
	mg/kg eq	%TRR	mg/kg eq	%TRR	mg/kg eq	%TRR	mg/kg eq	%TRR	mg/kg eq	%TRR
TRR	0.30	100%	0.23	100%	0.047	100%	0.10	100%	0.20	100%
M1	0.008	2.7%	0.012	5.2%	0.009	19%	0.013	13%	0.007	3.6%
M2	0.000	0.0%	0.000	0.0%	0.000	0.0%	0.016	16%	0.000	0.0%
M3	0.006	2.0%	0.000	0.0%	0.009	19%	0.010	9.8%	0.009	4.6%
M4	0.000	0.0%	0.000	0.0%	0.000	0.0%	0.010	9.8%	0.000	0.0%
Polar [a]	0.092	31%	0.10	44%	0.000	0.0%	0.002	2.0%	0.004	2.0%
Lipid conjugated	0.015	5.0%	0.000	0.0%	0.000	0.0%	0.000	0.0%	0.073	37%
Lipid	0.000	0.0%	0.007	3.1%	0.000	0.0%	0.001	1.0%	0.000	0.0%
Not analysed	0.000	0.0%	0.000	0.0%	0.004	8.5%	0.000	0.0%	0.005	2.6%
Enzyme released	0.14	46%	0.091	40%	0.017	36%	0.050	49%	0.095	48%
Remaining solids	0.041	14%	0.018	7.9%	0.009	19%	0.002	2.0%	0.004	2.0%
Total	0.30	100%	0.23	100%	0.048	102%	0.10	102%	0.20	100%

a multicomponent polar metabolites

M1 = ethylsulfonyl methylsulfonyl methane

M2 = (ethylsulfinyl) methyl methyl sulfone;

M3 = ethyl (methylsulfinyl)methyl sulfone

M4 = (ethylsulfinyl)(methylsulfinyl) methane

Plant metabolism

The Meeting received information on the fate of phorate in plants placed in phorate solutions, in cotton grown from seed treated with phorate, and in various plants after soil or foliar application of phorate. Characterization of metabolites was limited to root and foliar parts of young plants. Confined rotational crop studies gave information on the metabolite composition of mature crops (see environmental fate section). Experiments were carried out with ^{32}P labelled phorate or with phorate ^{14}C labelled at the methylene position (see Figure 1).

Plants placed in phorate solution

Red kidney bean seedlings, with their first trifoliate leaves, were placed in an emulsion of 500 mg/L ^{32}P-phorate solution (Bowman and Casida, 1958: PA-905-051). Specific activity of the undiluted compound was 18 mCi/g. Only the roots were in contact with the dipping solution. After 1 d, the roots were washed and the plants were transplanted into white sand. At 1, 4 and 12 d after application, the primary and secondary leaves from 25 plants were collected and analysed immediately.

The sampled leaves were homogenised with a mixture of chloroform and water (100:20, v/v). The chloroform fraction was chromatographed on celite-isooctane-MeOH columns and the peaks were characterized by the elution positions and partitioning properties between hexane, acetone and water (5:4:7, v/v/v). The water fraction was chromatographed on anion-exchange columns and the elution positions were determined by colorimetric total phosphorus analysis and coelution with reference standards for O,O-diethyl phosphoric, phosphorothioic and phosphorodithioic acids.

Results are shown in Table 5. The primary metabolites were phorate sulfoxide and/or phorate sulfone, which could not be separated on the columns used. Small amounts of phoratoxon sulfoxide and/or phoratoxon sulfone and unchanged phorate were also found. No phoratoxon was found. The hydrolysis products formed were phosphoric acid, the diethyl esters of phosphoric acid, phosphorothioic acid and phosphorodithioic acid.

Information on radiochemical purity, quantitative data on parent and metabolites (expressed as %TRR and mg/kg eq) is not available and administration of phorate does not reflect actual application methods.

Table 5. Metabolic profile of leaves from kidney bean seedlings, dipped in ^{32}P-phorate solution.

Fraction	Metabolite	1 d %TER	4 d %TER	12 d %TER
chloroform	phorate	2.8%	0.4%	0.5%
	phorate sulfoxide and/or phorate sulfone	76%	81%	64%
	phoratoxon sulfoxide and/or phoratoxon sulfone	0.0%	0.5%	8.5%
water	phosphoric acid	0.6%	2.6%	1.6%
	O,O-diethyl phosphoric acid	1.7%	4.0%	8.4%
	O,O-diethyl phosphorothioic acid	8.1%	9.2%	13%
	O,O-diethyl phosphorodithioic acid	7.6%	1.5%	3.0%
	Unknown	3.0%	0.7%	1.3%
total		100%	100%	100%

%TER = percentage total extracted residue. The percentage solids are not stated and therefore %TRR is unknown.

Plants grown from phorate-treated seeds

A mixture of ^{32}P-phorate and charcoal was coated on cotton seeds wetted with 2% methylcellulose at a concentration of 160 kg ai/t or 320 kg ai/t (Bowman and Casida, 1957: PA-905-046). Subsequently, seeds were treated by spraying and drying with 5% methylcellulose several times to form a hard coat. Treated seeds were planted and cotton plants were sampled at 3.9, 7.4 and 10.7 weeks after planting (Wisconsin; seeds treated at 160 kg ai/t) or 16 weeks after planting (Oklahoma; seeds treated at 160 kg ai/t or 320 kg ai/t). In addition, cotton plants were grown for 2 weeks from seed treated with 40 kg ai/t of seed and the foliage was sampled for identification of metabolites. Information on storage conditions is not available.

Macerated foliage samples were extracted with chloroform, which was fractionated into hexane and acetone-water. Macerated seeds were extracted using diethyl ether in a Soxhlet for 8 hrs. The remaining seed solids were extracted with chloroform. Both seed extracts were combined and fractionated with hexane and acetone-water. Extracts were analysed for ^{32}P. Extracts of cotton foliage were fractionated on Celite columns and identity of metabolites was confirmed by IR.

Distribution of ^{32}P residues in extracts of cotton is shown in Table 6. Total ^{32}P residues were less than 0.03 mg/kg eq in seeds maturing from plants grown from seed treated with 320 kg ai/t. The residues isolated from the foliage consisted of phorate sulfoxide and phorate sulfone (ratio 61:39) and phoratoxon sulfoxide and phoratoxon sulfone (ratio 70:30). Parent itself was not identified because of interference from plant pigments. Phoratoxon was not found.

Information on radiochemical purity, specific activity, plant cultivation conditions, growth stages at harvest, pre-harvest intervals, quantitative data on parent and metabolites (expressed as %TRR) is not available. The administration of phorate did not reflect actual application methods.

Table 6. Total ^{32}P residues in cotton following seed treatment.

Plant part	foliage	foliage	leaves	squares	seed	seed	leaves
Treatment (kg ai/t)	160	160	160	160	160	320	320
Weeks after planting	3.9	7.4	10.7	10.7	16	16	16
Hexane (mg/kg eq)	0.27	< 0.0006	< 0.0006	< 0.006	-	< 0.030	< 0.005
Acetone:water (mg/kg eq)	0.29	0.0036	< 0.0006	< 0.006	< 0.025	< 0.030	< 0.005
Hydrolysis products[1] (mg/kg eq)	0.54	0.019	< 0.0006	< 0.006	-	-	-
Unextracted residue (mg/kg eq)	0.93	0.035	< 0.0006	< 0.006	-	-	-
Total residue (mg/kg eq)	2.0	0.058	< 0.0006	< 0.006	< 0.03	< 0.03	< 0.005

[1] Residues remaining in the water phase after chloroform extraction.

Soil and foliar application of phorate

Study 1. The bases of young cotton plants, lemon seedlings and alfalfa seedlings were treated with a topical application of ^{32}P-labelled phorate solution (Metcalf *et al.*, 1957: PA-905-047). The radioactive purity was > 99%. At various intervals after application (up to 14–17 d) upper leaves were sampled.

The sampled leaves were homogenized with a water/chloroform mixture (1:1 v/v) and radioactivity in water and chloroform layers was measured. The chloroform extract was evaporated to dryness, redissolved in acetone and separated by paper chromatography. Metabolites were identified by retention times for reference compounds (parent, phorate sulfoxide, phorate sulfone, phoratoxon, phoratoxon sulfoxide and phoratoxon sulfone).

In the study report, results were presented as graphs. Values mentioned below, were read from the graphs by the present reviewer.

The rate of accumulation increased with time (day 1 to 4), until a maximum of about 95 mg/kg eq in cotton leaves was found at day 4. Thereafter, the accumulation rate decreased to 60 and 55 mg/kg eq at day 7 and day 14 after treatment, respectively. Radioactivity in the water layer increased with time at a maximum radioactive distribution of 1:1 in chloroform:water for day 7 and day 14.

Parent and four metabolites could be identified in the chloroform layer of cotton, lemon and alfalfa leaves (day 1–17). For cotton leaves, parent was found up to 5 d and never exceeded 5% of the radioactivity in the chloroform layer. Phorate sulfoxide reached a maximum of 85% radioactivity in the chloroform layer of cotton leaves at day 1 after application and thereafter decreased to 35 % at day 14. Phorate sulfone, phoratoxon sulfoxide and phoratoxon sulfone increased with time at up to 35%, 15% and 10% radioactivity in the chloroform layer at day 14, respectively. Phoratoxon was not found at any timepoint.

Information on specific activity, application rate and quantitative data on parent and metabolites (expressed as %TRR and mg/kg eq) is not available.

Study 2. Beans, beets, cabbage, carrots, lettuce and peas were treated with radiolabelled ^{32}P-phorate using both a foliar and a soil application (Bowman and Casida, 1957: PA-905-046). Applications were made with an EC formulation at a rate of 1.12 kg ai/ha. Foliage was wetted to the point of run-off. Soil treatments were made at the base of the plants. The vegetable foliage was sampled at 2 hrs and 1, 2, 4, 8, 17 and 32 DAT. Samples were stored at -10 °C until analysis (storage period not stated). In addition pea plants were soil treated and the foliage was sampled at 14 DAT for identification of metabolites.

Residues were extracted from macerated plant samples using chloroform, which was fractionated into hexane and acetone-water. Extracts were analysed for ^{32}P and/or anti-acetylcholinesterase activity. Extracts of pea foliage were fractionated on Celite columns and identity of metabolites was confirmed by IR.

Distribution of ^{32}P radioactivity and anti-acetylcholinesterase activity in extracts from beans, beets, cabbage, carrots, lettuce and peas in the same field plot are presented in Tables 7 and 8 as average values. Values for individual vegetables are not available. Anti-acetylcholinesterase activity increased for about the first 4 d and then declined, but inhibitors still persisted for 20 to 30 d. Residues became more polar in time.

The residues isolated from the pea foliage consisted of phorate sulfoxide and phorate sulfone (ratio 80:20). Parent itself was not identified because of interference from plant pigments. Phoratoxon was not found.

Phorate itself is a weak acetylcholinesterase inhibitor, but when applied to plants, phorate is very rapidly converted to potent anti-acetylcholinesterase agents. Anti-acetylcholinesterase activity (pI_{50}) is 3.2 for parent, 3.4 for phorate sulfone, 5.0 for phorate sulfoxide, 5.9 for phorate oxon, 6.8 for phorate oxon sulfoxide and 7.0 for phorate sulfone. Anti-acetylcholinesterase activity increased when P=S was replaced by P=O, and increased further upon successive oxidation to sulfoxide and sulfone.

Information on radiochemical purity, specific activity, plant cultivation conditions, growth stages at treatment and at harvest and quantitative data on parent and metabolites (expressed as %TRR and mg/kg eq) is not available.

Table 7. Distribution of ^{32}P residues in extracts from vegetable crops [1] following foliar application.

DAT	0.1	1	2	4	8	17	32
Hexane (mg/kg eq)	6.8	2.8	2.5	1.7	0.90	0.44	0.040
Acetone:water (mg/kg eq)	2.6	2.4	1.7	1.4	0.59	0.067	0.003
Hydrolysis products [2] (mg/kg eq)	0.28	0.37	0.62	0.85	1.3	0.43	0.27
Unextracted residue (mg/kg eq)	1.4	1.0	0.81	1.6	1.5	1.1	2.3
AChE Activity, 50% inhibition							
Plant tissue (g) [3]	1.3	0.47	0.59	0.54	1.6	>2.2	>2.2
pI_{50} metabolites [4]	5.4	6.1	6.3	6.6	6.1	<7.2	<7.4

1 Results are average of values from beans, beets, cabbage, carrots, lettuce and peas in the same field plot.
2 Residues remaining in the water phase after chloroform extraction.
3 Amount of plant material containing enough metabolites for 50% inhibition. Results are based on chloroform extracts.
4 Negative logarithm of molar concentration effecting 50% inhibition. Results are based on chloroform extracts.

Table 8. Distribution of ^{32}P residues in extracts from vegetable crops[1] following soil application.

DAT	0	1	2	4	8	17	32
Hexane (mg/kg eq)	0.82	0.34	0.40	0.26	0.15	0.049	0.026
Acetone:water (mg/kg eq)	0.12	0.31	0.56	0.36	0.18	0.047	0.003
Hydrolysis products [2] (mg/kg eq)	0.052	0.12	0.13	0.24	0.25	0.21	0.110

DAT	0	1	2	4	8	17	32
Unextracted residue (mg/kg eq)	0.15	0.16	0.42	1.2	0.46	0.11	0.078
AChE Activity, 50% inhibition							
Plant tissue (g) [3]	1.8	0.94	1.3	1.2	1.3	>2.9	>3.0
pI_{50} metabolites[4]	6. 9	7.3	6.7	6.7	7.0	7.2	7.2

1 Results are average of values from beans, beets, cabbage, carrots, lettuce and peas in the same field plot.

2 Residues remaining in the water phase after chloroform extraction.

3 Amount of plant material containing enough metabolites for 50% inhibition. Results are based on chloroform extracts.

4 Negative logarithm of molar concentration effecting 50% inhibition. Results are based on chloroform extracts.

Study 3. Effects of soil treatments on the translocation and metabolism of ^{14}C-phorate in maize seedlings were investigated (Schulz *et al.*, 1976: PA-905-049). Experiments with the herbicide Eptam (EPTC, S-ethyl dipropylthiocarbamate) and its maize antidote (Stauffer R-25788, N-diallyl-2,2-dichloroacetamide) were not summarized.

Phorate was ^{14}C labelled at the methylene position with a specific activity of 9.7 mCi/mmol. Three cartons containing sand (0.6% organic matter (om), 3% clay) were treated with 2 mg ai/kg ^{14}C-phorate. Immediately after soil treatment 8 germinated maize seeds were planted in each test soil. The cartons were kept at 21-24 °C under a bank of lamps on a 12 hr photoperiod. After 18 d plants had grown to a length of 25-29 cm and leaves were cut 1 cm above soil surface. The roots were removed from the soil and rinsed with tap water. Storage conditions are not stated.

The soils and plant materials were extracted twice with a 1:1 mixture of MeOH-acetone followed by an extraction with a 1:1:1 mixture of benzene-MeOH-acetone. Extracts were combined and partitioned into benzene and water soluble fractions. ^{14}C residues in extracts and remaining solids were determined by LSC or combustion LSC. Benzene extracts were fractionated by GC and TLC.

Of the applied radioactivity 77% was recovered: 71% in soil, 4.0 % in maize greens and 1.8% in maize roots (see Table 9). Phorate and phorate sulfoxide were the major compounds present in the benzene extracts from soil; the remainder was found to be phorate sulfone (see Table 10). No phoratoxon, phoratoxon sulfoxide or phoratoxon sulfone was found in benzene extracts of soil. Phorate sulfoxide, phorate sulfone and phoratoxon sulfoxide were the only compounds present in the benzene extracts from maize greens (see Table 10). No phorate, phoratoxon or phoratoxon sulfone was found in benzene extracts of maize greens.

Table 9. Distribution of ^{14}C residues in extracts from maize seedlings and soil following soil application.

Extraction phase	Maize greens		Maize roots		Soil	
	%TAR[a]	%TRR[b]	%TAR[a]	%TRR[b]	%TAR[a]	%TRR[b]
Benzene	2.1 ± 0.39	54%	0.70 ± 0.26	38%	68 ± 1.12	96%
Water	1.3 ± 0.06	32%	0.70 ± 0.09	38%	0.27 ± 0.01	0.4%
Solids	0.62 ± 0.17	16%	0.44 ± 0.00	24%	2.8 ± 0.57	3.9%
Total	4.0 ± 0.62	100%	1.8 ± 0.35	100%	71 ± 1.47	100%

a mean and standard deviation

b calculated by present reviewer from distribution within %TAR

Table 10. Characterization of benzene extracts from maize greens and soil following soil application.

Compound	Maize greens		Soil	
	mg/kg eq[a]	%TRR[b]	mg/kg eq[a]	%TRR[b]
Phorate	0.00 ± 0.00	0.0%	0.55 ± 0.02	42%
Phorate sulfoxide	3.4 ± 0.80	32%	0.62 ± 0.04	48%
Phorate sulfone	1.8 ± 0.17	16%	0.08 ± 0.01	6.1%
Phoratoxon sulfoxide	0.54 ± 0.08	5.0%	-	-
Total	5.7 ± 0.87	54%	1.2 ± 0.02	96%

a mean and standard deviation

b calculated by present reviewer from %TAR results and distribution within benzene extracts

Study 4. Effects of soil treatments on the translocation and metabolism of ^{14}C-phorate in oat seedlings were investigated (Fuhremann and Lichtenstein, 1980: PA-905-044). Phorate was ^{14}C labelled at the methylene position with a specific activity of 1.3 mCi/mmol and a radiochemical purity of 97%. Soils were kept in cartons in a growth chamber. A silt loam soil (pH=6.0, 4.7% om, 24% clay) was treated with 4 mg ai/kg, while the sandy soil (pH 5.6, 0.6% om, 3.0% clay) was treated with 2 mg ai/kg as ^{14}C-phorate. One day after soil treatment 25 germinated oat seeds were planted in each test soil. The cartons were kept at 28 °C under a bank of lamps on a 15 hr light, 9 hr dark cycle. After 13 days, leaves were cut at 1 cm above the soil surface and roots and soil were separated. Leaves and roots were rinsed with tap water; soil was dried for 2 days. Storage conditions were not stated.

The soil and plant materials were extracted with a 1:1:1 mixture of acetone-MeOH-benzene. Extracts were evaporated to dryness and partitioned into benzene and water soluble fractions. ^{14}C residues in extracts and remaining solids were determined by LSC or combustion LSC. Benzene extracts were cleaned-up and fractionated by TLC against reference standards (parent, phorate sulfoxide, phorate sulfone, phoratoxon, phoratoxon sulfoxide and phoratoxon sulfone). Identity of TLC isolated compounds was confirmed by GC-NPD.

For the sandy soil system 59% of total applied radioactivity was recovered: 26% in soil, 3.5% in roots and 30% in oat greens (see Table 11). For the silt loam soil system 76% of total applied radioactivity was recovered: 68% in soil, 0.5% in roots and 7.4% in oat greens (see Table 11). The ^{14}C residues remaining in silt loam soil were higher than the ^{14}C residues remaining in sandy soil, while oats growing in sandy soil contained more radiocarbon than those grown in loam soil.

Phorate, phorate sulfoxide and phorate sulfone were the major compounds present in the benzene extracts from oat seedlings and soil; the remainder was unknown compounds (see Table 12).

Table 11. Distribution of ^{14}C residues in extracts from oat seedlings and soil following soil application.

Soil	Extraction phase	Oat greens		Oat roots		Soil	
		%TAR[a]	%TRR[b]	%TAR[a]	%TRR[b]	%TAR[a]	%TRR[b]
silt loam	Benzene	2.1 ± 0.6	28%	0.2 ± 0.1	40%	52 ± 3.9	77%
	Water	4.5 ± 0.7	61%	0.0 ± 0.0	0.0%	2.7 ± 0.1	4.0%
	Solids	0.8 ± 0.1	11%	0.3 ± 0.1	60%	13 ± 0.8	19%
	Total	7.4	100%	0.5	100%	68	100%
sandy	Benzene	15 ± 1.0	51%	0.4 ± 0.0	11%	20 ± 1.2	79%
	Water	11 ± 0.6	38%	0.4 ± 0.1	11%	1.0 ± 0.1	3.9%
	Solids	3.2 ± 0.4	11%	2.7 ± 0.1	77%	4.5 ± 0.1	17%
	Total	30	100%	3.5	100%	26	100%

[a] mean and standard deviation

[b] calculated by present reviewer from distribution within %TAR.

Table 12 Characterization of benzene extracts from oat seedlings and soil following soil application

	Silt loam soil			Sandy soil		
Compound	Oat greens	Oat roots	Soil	Oat greens	Oat roots	Soil
	%TRR[a]	%TRR[a]	%TRR[a]	%TRR[a]	%TRR[a]	%TRR[a]
Phorate	0.0%	0.0%	3.4%	0.0%	0.0%	14%
Phorate sulfoxide [b]	6.3%	20%	34%	24%	5.7%	45%
Phorate sulfone [b]	7.9%	20%	37%	12%	5.7%	13%
Unknown	14%	0.0%	1.7%	15%	0.0%	6.4%
Total	28%	40%	77%	51%	11%	79%

[a] calculated by present reviewer from distribution within %TAR.

[b] identity confirmed by GC-NPD

Study 5. Extraction efficiency was tested for potatoes, carrots and radishes, which had been soil treated with ^{14}C-phorate (Sonobe *et al*., 1982: PA-905-052). Plants were grown from seed (or seed potatoes) in pots in a silt loam soil (no details provided). When plants began to produce edible parts, pots were placed in a greenhouse with temperature control for ^{14}C-phorate treatment. Phorate was ^{14}C labelled at the methylene position with a specific activity of 3.26 mCi/mmol (undiluted) or 1.37 mCi/mmol (diluted) and a radiochemical purity of 99%. An aqueous suspension of ^{14}C-phorate was pipetted onto both the soil and the partly exposed roots/tubers at an application rate equivalent to 2.25-3.35 kg ai/ha. Roots/tubers were harvested 5, 10, and 15 DAT and were rinsed with tap water. Samples were stored at -20 °C for an unstated period.

Roots were extracted either with MeOH or with ACN (four times) and combined extracts were partitioned into DCM and water soluble fractions. Solids were Sohlet extracted for 16 hrs in a chloroform-MeOH (9:1, v/v). ^{14}C residues in extracts and remaining solids were determined by LSC or combustion LSC. DCM extracts were fractionated by TLC against reference standards (parent, phorate sulfoxide, phorate sulfone, phoratoxon, phoratoxon sulfoxide and phoratoxon sulfone). Identity of TLC isolated compounds was confirmed by GC-FPD.

In the study report, results were presented as graphs. Values mentioned below, are taken from the text in the study report and were partly read from the graphs by the present reviewer.

Total recovered ^{14}C residues (TRR) in the roots/tubers ranged from 0.86 to 12.6 mg/kg eq. MeOH was found to be the better solvent, in particular for potatoes. Extraction efficiency after four extractions ranged from 84%–96% TRR for MeOH and 72%–93% TRR for ACN. A great difference in the nature of ^{14}C residues was found between carrots and the other two root crops. With carrots, more than 96% of the radioactivity in the MeOH or ACN extracts was DCM extractable, and the ratio of water soluble ^{14}C residues did not increase with increasing incorporation time. With potatoes and radishes, the ratio of water soluble ^{14}C residues was much greater than with carrots and this ratio increased with time. At day 15, 95.8% of the radioactivity in the MeOH extract of carrots was partitioned into DCM, while this was 46.4% and 35.3% for potatoes and radishes, respectively. For potatoes and radishes, MeOH extracted more water-soluble ^{14}C residues than ACN.

Phorate sulfoxide (20–75%) and phorate sulfone (15–70%) were the major compounds present in DCM extracts from potatoes and radishes; parent (10–25%), phorate sulfoxide (50–60%) and phorate sulfone (10–25%) were the major compounds present in the DCM extracts from carrots (expressed as percent ^{14}C in DCM extracts). Phorate and phorate sulfoxide decreased with time, while phorate sulfone increased with time. Phoratoxon, phoratoxon sulfoxide and phoratoxon sulfone were found at trace levels (< 3.2% of ^{14}C in DCM extract). The six phorate residues accounted for 99% of ^{14}C in DCM extracts of all three crops.

With carrots and radishes, little ^{14}C was removed by Soxhlet extraction (0.83–3.0% TRR). With potatoes, a low amount of 14C was removed by Soxhlet extraction (3.0%–10% TRR). Carrots have the smallest amount of remaining solids (3.1–4.3% TRR) and potatoes and radishes have more solids (7.2% to 22% TRR), increasing as the incorporation period increases.

Study 6. Effects of light intensity and temperature on the translocation and metabolism of ^{14}C-phorate in soil treated oat, pea, and maize plants were investigated (Anderegg and Lichtenstein, 1984: PA-905-050). Phorate was ^{14}C labelled at the methylene position with a specific activity of 9.7 mCi/mmol and a radiochemical purity of 97%. Soils were kept in cartons in a growth chamber. A sandy soil (pH 5.6, 0.6% om, 3.0% clay) was treated with ^{14}C-phorate at 1 mg ai/kg. Eight maize seedlings (variety Funk G4444-0900), 25 oat seedlings (cv. Lodi) and 8 pea seedlings (cv. Alaska) were planted in each test soil. The cartons were kept at temperatures of 13 and 28 °C under a bank of lamps on a 15 hr light, 9 hr dark cycle with light intensities of 500 and 3000 ft-c). After 10 d (oats, maize) or 12 d (peas), plant roots, plant tops and soil were separated. In a separate experiment, oat seedlings were grown for 5 d in an open system and then for 10 d in a closed system under bell jars, using the same temperature and light intensity gradients. Volatile ^{14}C evolving from the plant-soil system was trapped in a polyurethane plug and a NaOH trap. Storage conditions are not stated.

The soils and plant materials were extracted with a 1:1:1 mixture of acetone-MeOH-benzene. Extracts were evaporated to dryness and partitioned into benzene and water soluble fractions. ^{14}C residues in extracts and remaining solids were determined by LSC or combustion LSC. Benzene extracts were cleaned-up and fractionated by TLC against reference standards (parent, phorate sulfoxide, phorate sulfone, phoratoxon, phoratoxon sulfoxide and phoratoxon sulfone). Identity of TLC isolated compounds was confirmed by GC-NPD.

In the open systems, 53–77% of the applied radioactivity was recovered, while 85–90% of the applied system was recovered in the closed system. It is possible that 10-15% of the applied radioactivity is lost during the 5 day period that the closed system was open. No volatile lipid-soluble carbon was recovered from the polyurethane plug, while 1.1% to 7.3% TAR was recovered as $^{14}CO_2$ in the NaOH trap.

At low temperatures (13 °C) and low light intensity (500 ft-c) 50–60% TAR remained in the soil and 4–13% TAR was translocated into plant tops, while at the extreme condition of 28 °C and 3000 ft-c only 12–42% TAR remained in the soil and 10–30% TAR was translocated into plant tops (results expressed as absolute amounts, not on a weight basis, because of growth differences in plants).

Distribution of radioactivity in the different extracts is shown in Table 13. Higher light intensity affected the metabolism of translocated ^{14}C compounds primarily at 28 °C. Higher temperatures caused in most cases an increase in the uptake of ^{14}C compounds from soil. The relative distribution of benzene-soluble, water-soluble and bound radiocarbon was quite similar in all plants under all experimental conditions.

Phorate sulfoxide was the major compound present in plant tops and soil (see Table 14). Contrary to soils, parent was not found in plant tops. Additional compounds found in plant tops and soil were phorate sulfone, phoratoxon sulfoxide and phoratoxon sulfone.

Table 13. Distribution of ^{14}C residues in extracts from plant tops and soil following soil application.

Crop	Extraction phase	Tops	Tops	Tops	Tops	Soil	Soil
		13 °C 500 ft-c	13 °C 3000 ft-c	28 °C 500 ft-c	28 °C 3000 ft-c	13 °C 500 ft-c	28 °C 3000 ft-c
Oats	Benzene (%TRR)	50	54	47	38	87	51
	Water (% TRR)	44	40	42	51	3	4
	Solids (%TRR)	6	6	11	11	10	45
	Total (%TRR)	100	100	100	100	100	100
	Total (%TAR)[a]	2.8 ± 0.46	4.1 ± 0.14	5.6 ± 1.2	7.6 ± 0.19	50 ± 1.4	15 ± 2.6
Peas	Benzene(%TRR)	60	55	59	48	84	72
	Water (% TRR)	23	23	29	29	3	4
	Solids (%TRR)	17	22	12	23	13	24
	Total (%TRR)	100	100	100	100	100	100
	Total (%TAR)[a]	1.6 ± 0.16	1.6 ± 0.24	4.3 ± 0.60	6.5 ± 1.1	55 ± 2.0	42 ± 1.3
Maize	Benzene(%TRR)	60	55	47	48	91	58
	Water (% TRR)	34	39	46	41	3	3
	Solids (%TRR)	6	6	7	11	6	39
	Total (%TRR)	100	100	100	100	100	100
	Total (%TAR)[a]	2.0 ± 0.06	2.0 ± 0.16	1.8 ± 0.17	3.1 ± 0.29	60 ± 5.9	11 ± 0.75

a mean and standard deviation of three replicates, results are expressed per g plant tops

Table 14. Characterization of benzene extracts from plant tops and soil following soil application.

Crop	Compound	Tops	Tops	Soil	Soil
		13 °C 500 ft-c	28 °C 3000 ft-c	13 °C 500 ft-c	28 °C 3000 ft-c
Oats	Phorate (%TRR) [a]	0.0	0.0	7.8	13
	Phorate sulfoxide (%TRR) [a]	28	15	61	21
	Phorate sulfone (%TRR) [a]	14	10	17	16
	Phoratoxon sulfoxide (%TRR) [a]	3.5	4.9	0.9	0.5
	Phoratoxon sulfone (%TRR) [a]	3.5	7.6	< 0.9	0.5
	Total (%TRR)	50	38	87	51
Peas	Phorate (%TRR) [a]	0.0	0.0	5.0	2.9
	Phorate sulfoxide (%TRR) [a]	40	25	56	37
	Phorate sulfone (%TRR) [a]	13	15	21	31
	Phoratoxon sulfoxide (%TRR) [a]	6.6	7.7	0.8	< 0.4
	Phoratoxon sulfone (%TRR) [a]	0.0	0.0	0.8	< 0.4
	Total (%TRR)	60	48	84	72
Maize	Phorate (%TRR) [a]	0.0	0.0	16	19
	Phorate sulfoxide (%TRR) [a]	33	19	63	24
	Phorate sulfone (%TRR) [a]	22	16	11	14
	Phoratoxon sulfoxide (%TRR) [a]	5.4	6.2	< 0.5	0.0
	Phoratoxon sulfone (%TRR) [a]	0.0	6.2	< 0.5	1.2
	Total (%TRR)	60	48	91	58

a results are expressed per g fresh weight (plant tops) or as absolute weight (soil)
b calculated by present reviewer from %TRR results in benzene and distribution within benzene extracts.

Environmental fate in soil

The Meeting received information on laboratory soil degradation and field and confined rotational crop studies. Experiments were carried out with phorate ^{14}C labelled at the methylene position (see Figure 1).

Aerobic soil degradation studies

Study 1. Phorate, phorate sulfoxide and phorate sulfone were applied at a concentration of 10 mg ai/kg dw soil, as individual components (Harris and Chapman, 1980: PA-905-042). Test soils were: sand (pH 7.6, 0.5% organic matter, % clay ns) and muck (pH 7.6, 49% om, % clay ns). Soil samples were placed in uncovered plastic pots, which were brought up to field moisture capacity (5% water) weekly. Tests were done in environmental chambers maintained at 27 ± 1 °C, 65 ± 5% relative humidity and 24 hr photoperiod. Samples were taken at intervals up to 48 weeks. Homogenised soil samples were extracted with acetone/chloroform (1:2, v/v). After clean-up, the chloroform phase was column chromatographed for fractions containing phorate, phorate sulfoxide and phorate sulfone. Each fraction was analysed by GC with a rubidium sulfate alkali flame detector.

In the study report, results were presented as graphs, and therefore quantitative values could not be presented as a table for the present evaluation. Values mentioned below, are taken from the text of the study report.

In sandy soil, phorate degraded rapidly, declining to 5% of the initial application within 4 weeks after treatment. Phorate sulfoxide built up rapidly reaching 25% of the initial application in 2 weeks. This was followed by conversion to phorate sulfone which peaked at 35% of the initial application in 5 weeks. Forty eight weeks after treatment, 0.2% of the initial phorate application was present as parent, 0.9% as phorate sulfoxide and 6.7% as phorate sulfone.

In sandy soil, phorate sulfoxide degraded more slowly than phorate, declining to 5% of the original application in 8 weeks after treatment. Phorate sulfone built up rapidly to 54% of the initial application. A small amount of the applied phorate sulfoxide was reduced to phorate: the phorate level on the day of treatment was 0.9% of the initial application and this level increased to 3.5% of the initial application 5 DAT, declining thereafter. Forty-eight weeks after treatment, none of the initial phorate sulfoxide application was present as parent, 0.7% was still present as the phorate sulfoxide and 6.5% was present as phorate sulfone.

In sandy soil, phorate sulfone was the most persistent of the three compounds, declining to 5% of the initial application within 40 weeks after treatment. A small amount of the applied phorate sulfone was reduced to phorate sulfoxide, with a peak of 2.2% of the initial application 1 week after application. Forty-eight weeks after treatment, none of the initial phorate sulfone application was present as parent or as phorate sulfoxide, but 3.6% was still present as phorate sulfone.

Similar results were obtained for the muck soil. However, conversion of phorate to phorate sulfoxide and phorate sulfone was faster than in sandy soil (quantitative values not stated). Phorate sulfone was the most persistent > phorate sulfoxide > phorate. It is likely that faster degradation in muck soil occurred because the sand dried out quickly, despite weekly watering, thus affecting both the rate of volatilization and microbial activity.

Study 2. The degradation route of methylene-^{14}C-Phorate was investigated in a sandy loam soil incubated under aerobic conditions for a period of 9 months (Lavin, 1987: PA-620-002). The specific activity was 10,595 dpm/µg, the radioactive purity was not stated. Phorate was applied at a nominal rate of 1.39 mg ai/kg dw soil. Soil characteristics are summarized in Table 16. Soil was kept in environmental control chambers maintained at an average temperature of 25°C in the dark under continuous ventilation with moistened air. Moisture levels in the control and treated soils ranged from 60–77% and 48–74% of field capacity (11.05% at 1/3 bar), respectively. Systems were connected to four gas washing bottles, containing ethylene glycol, 1 N H_2SO_4 and two 1 N KOH traps respectively, to trap radioactive volatiles from the reaction vessels. Soil was sampled on various timepoints. Storage conditions were not stated.

Soil samples were extracted with ACN, followed by a reflux extraction with MeOH/water (80:20) for 15 hrs. Soils from day 60, 125, 182 and 273 were subsequently extracted with 2% HCl/MeOH under reflux for approximately 13 hrs. The 92, 125, 182 and 273 day samples were extracted with 0.1N KOH at room temperature overnight. Acid and base extracts were partitioned into DCM. Soil samples, extracts, solids and trapping solutions were analysed by (combustion) LSC for total radioactivity. Extracts were analysed using TLC with standard reference compounds for phorate, phorate sulfoxide, phorate sulfone, phoratoxon, phoratoxon sulfoxide and phoratoxon sulfone.

Results are shown in Table 15. Results are expressed as percentage of initial dose measured at day zero (% IDM). As the study progressed, it was apparent that there was some loss of radioactivity. The mass balance ranged from 98%–103% IDM in the first month of the study and declined to 73%–92% IDM for the rest of the study period.

The degradation of phorate was relatively rapid (half-life was 3.0 days). Levels of phorate had degraded to 2% IDM by day 17. Phorate was not detectable by day 31 when analysed by TLC.

Three major metabolites were formed during the study: phorate sulfoxide, phorate sulfone and CO2. A trace of a fourth species occurred only at nine months (1.7% IDM). The first metabolite to form was phorate sulfoxide, which in turn was oxidised further to phorate sulfone.

There was a significant evolution of radioactivity trapped in KOH (29.5% IDM cumulative after 9 months). Approximately 78% of the radioactivity in a composite sample of the KOH trap was precipitated from solution when $BaCl_2$ was added. The precipitated $BaCO_3$ confirms that the volatile radioactivity was in the form of $^{14}CO_2$.

The half-life of phorate sulfoxide (day 31 to 9 month) was 74.9 d. The day 0 analysis showed that 27.4% IDM was present as phorate sulfoxide. Phorate sulfoxide increased to a peak value (50.6%

IDM) at day 6. The appearance of phorate sulfone indicated that as phorate sulfoxide was forming it was further oxidising to phorate sulfone.

The half-life for phorate sulfone could not be estimated due to the increasing difficulties with extraction and since it was being formed and degraded simultaneously. Phorate sulfone appeared at time 0 (1.7% IDM) and increased until day 60 to a peak value of 54% IDM. Phorate sulfone gradually decreased over the remainder of the study. This coincides with the decreased amount of radioactivity characterised. It is therefore possible that there could be some loss of phorate sulfone during exposure to the re-extraction conditions.

Table 15. ^{14}C mass distribution of phorate during aerobic degradation in soil expressed as %IDM (day 0 TRR 1.22 mg/kg eq).

DAT	TRR	Extracts ^{a} as %IDM						Solids	Volatile traps, cumulative, %IDM			Total
	mg/kg eq	Total	P	P-SO	P-SO2	unk ^{a}	TLC origin	%IDM	ethylene glycol	H_2SO_4	KOH	%IDM
0	1.22	100	70	27	1.7	1.2	0.0	0.2	0.0	0.0	0.0	100
1	1.24	101	55	39	2.3	4.5	0.0	0.2	0.0	0.0	0.5	102
3	1.19	95	34	45	10	1.5	4.0	1.1	0.0	0.0	1.8	98
6	1.22	95	13	51	28	1.5	1.4	2.4	0.0	0.0	2.7	100
9	1.20	92	5.0	44	40	1.2	1.8	3.3	0.1	0.0	3.2	98
13	1.25	93	2.3	41	47	2.5	0.0	5.4	0.1	0.0	3.9	103
17	1.22	91	2.0	37	48	3.3	0.0	4.5	0.2	0.0	4.5	100
31	1.24	85	0.0	29	54	0.0	1.8	10	0.2	0.0	6.3	102
60	1.11	76	0.0	18	54	0.5	3.2	5.6	0.4	0.0	8.9	91
92	1.20	81	0.0	14	46	1.2	6.5	4.5	0.4	0.0	12	85
120	1.12	61	0.0	6.9	47	2.0	4.9	15.0	0.5	0.1	16	92
125	1.09	70	0.0	10	49	4.2	0.5	1.7	0.5	0.1	16	83
182	0.93	53	0.0	3.8	39	2.4	5.1	0.4	0.6	0.1	22	73
273	1.06	53	0.0	3.5	41	0.9 1.7 ^{b}	0.5	2.9	0.7	0.2	30	81

a = ^{14}C residues in ACN, MeOH/water, MeOH/HCl and 0.1 N KOH extracts

a = unknown compounds in extracts (no specific bands in TLC)

b = compound found in HCl-water extract

Table 16. Soil characteristics and degradation half life times for phorate and its soil metabolites.

Compound	Soil	Temp °C	om %	pH	CEC meq/ 100 g dw soil	clay %	moisture pF ^{a}	DT50 d	DT90 d
phorate	sandy loam	25	2.4	4.8	7.2	13	2.5-3.5	3	
phorate sulfoxide	sandy loam	25	2.4	4.8	7.2	13	2.5-3.5	75	
phorate sulfone	sandy loam	25	2.4	4.8	7.2	13	2.5-3.5	-	

a. Field capacity is 11.05% at 1/3 bar. Moisture during the experiment ranged from 5.34-8.20% for treated soils. This is equivalent to 48%-74% of the field capacity. The pF values were estimated by the reviewer, based on pF-curves of representative soils. At some timepoints during the test the soil has been too dry (pF >3.0).

Rotational crop studies

Study 1. Field accumulation studies were conducted in Ontario, Canada in 1980 on rotational crops (Harris and Chapman, 1980: PA-905-042). Small plots (2 m^2) were surrounded by fibreglass barriers 30 cm deep, dug into the ground to a depth of 20 cm. The soil in the plots was replaced to a depth of 20 cm with the test soil: sand (pH 7.6, 0.5% organic matter (om), % clay ns) and muck (pH 7.6, 49% om, % clay ns). Phorate EC was applied as a broadcast application at 3.4 kg ai/ha and incorporated into the top 7-8 cm of each soil. Immediately after treatment, radishes (cv. Red Boy) and carrots (cv. Super Nantes) were planted in the treated plots. A year later the plots were spaded to simulate ploughing and radishes and carrots were planted again. Soil core samples were taken at various intervals up to 76 weeks after treatment. Radishes and carrots were harvested 4 and 14 weeks after planting, respectively. Tops were removed and roots were washed to remove soil particles. Samples were blended and extracted on the day of sampling.

Homogenised soil and crop samples were extracted with acetone/chloroform (1:2, v/v for soil, 1:1, v/v for crops). After clean-up, the chloroform phase was column chromatographed for fractions containing phorate, phorate sulfoxide and phorate sulfone. Each fraction was analysed by GC with a rubidium sulfate alkali flame detector.

In the study report, results in soil were presented as graphs, and therefore quantitative values could not be presented as a table for the present evaluation. Values mentioned below, are taken from the text of the study report.

In sand, phorate (parent) concentration of 2.6 mg/kg eq declined rapidly to 15% of the initial application 1 week after treatment and to 1% after 4 weeks. Only traces (< 0.01 mg/kg eq) were found in the soil after 8 weeks. Phorate sulfoxide built up rapidly reaching 16% of the initial application 1 week after treatment and declining thereafter to 1% after 12 weeks. Phorate sulfone levels peaked at 15% of the initial application 4 weeks after treatment, and declined to < 1% after 23 weeks. One year after treatment, total phorate-related residues comprised < 1% of the initial application and consisted only of phorate sulfone. Seventy six weeks after treatment only traces (< 0.01 mg/kg eq) of the three compounds were present in the soil.

Greater conversion of phorate to phorate sulfoxide and phorate sulfone occurred in the muck as compared to the sand. Initial phorate (parent) concentration of 7.5 mg/kg eq declined rapidly to 17% of the initial application 1 week after treatment and < 1% after 8 weeks. Phorate sulfoxide reached a peak of 30% of the initial application 2 weeks after treatment and declined to < 1% after 16 weeks. Phorate sulfone peaked at 29% of the initial application after 12 weeks and declined to < 1% after 64 weeks. One year after treatment total phorate-related residues comprised 2% of the initial application. Seventy six weeks after treatment total phorate-related residues had declined to < 1%.

Results in crops are shown in Table 17. More than 99% and 98% of the applied phorate and its oxidation products disappeared from the sand and muck, respectively, within a year of treatment. Low amounts of phorate sulfoxide and phorate sulfone were found in radishes grown on both soils in the first year but no residues were present in the second year. No residues were found in carrots grown on either soil.

Table 17. Phorate-related residues in soil and rotational crops.

			Sandy soil			Muck soil		
Commodity	Rotation year	Sampling interval	phorate mg/kg eq	phorate sulfoxide mg/kg eq	phorate sulfone mg/kg eq	phorate mg/kg eq	phorate sulfoxide mg/kg eq	phorate sulfone mg/kg eq
soil	1	0 DAT	2.6	0.52	0.43	7.5	1.9	0.94
soil	2	46 WAT	< 0.01	< 0.01	0.02	< 0.01	0.02	0.19
radish roots	1	0 + 4 WAT	nd	0.18	0.04	nd	0.07	0.10
radish roots	2	46 + 4 WAT	nd	nd	nd	nd	nd	nd
carrot roots	1	0 + 14 WAT	nd	nd	nd	nd	nd	nd
carrot roots	2	46 + 14 WAT	-	-	-	-	-	-

WAT = weeks after treatment, nd = not detected (value for detection limit not stated), - not analysed

Study 2. Confined accumulation studies were conducted in the USA in 1986 on rotational crops (Chiu, 1987: PA-640-001 and Chiu, 1988: PA-640-002). Sandy loam soil (pH 5.7, 3.1% om, 8.4% clay) was treated with a surface application of ^{14}C-phorate at the rate of 1.68 kg ai/ha. Phorate was ^{13}C and ^{14}C labelled at the methylene position; the radiopurity was > 98%. The specific activity was 10.4 mCi/mmol for the undiluted substance and 13.3 mCi/g for the diluted active substance. The treated soil was located outside in a wire fenced area in Princeton, NJ, USA. After an ageing period of 1, 3, 12 and 15 months maize (Pioneer), beetroot (Early Wonder), lettuce (Ruby), spring wheat (Stoa), radish (Champion), were seeded in the treated soil. Because spring wheat failed to produce enough sample due to insect infestation, these experiments were repeated in 1987. Soil was sampled at various depths. Maize, lettuce and spring wheat were sampled by cutting the plants 1.3 cm above the soil level. Beetroot and radish samples were separated into green leaves and tubers. Mature wheat samples were separated in straw and grain. Mature maize samples were separated in fodder, cobs and kernels. All crop samples were rinsed with tap water and distilled water to remove soil particles. All samples were blended and stored frozen (temperature and duration not stated).

Soil and crop samples were extracted with MeOH/water (4:1 v/v). Radioactivity in soil, crops, extracts and solids was measured by (combustion) LSC. Some extracts were cleaned up by HPLC. Extracts were fractionated by HPLC or 1D- or 2D-TLC. Reference compounds used were parent, phorate sulfoxide, phorate sulfone, phoratoxon, phoratoxon sulfoxide, phoratoxon sulfone, and ethylsulfonyl methylsulfonyl methane-. In study report PA-640-002 reference compounds were extended with phoratoxon.

A decrease in residue levels in soil was seen over time (see Table 18). Most of the radioactivity remained in the top 7.5 cm of soil, indicating that phorate and its metabolites exhibited no appreciable leaching beyond a 15 cm depth of soil. Phorate was rapidly oxidized in the soil and was converted into phorate sulfone accounting for 66%, 26% and 6.8% TRR in samples from 1, 3 and 12 months after treatment, respectively. Only 0.2% TRR parent was found in the soil extract one month after treatment. Other metabolites identified were phorate sulfoxide, phoratoxon, phoratoxon sulfoxide, phoratoxon sulfone and ethylsulfonyl methylsulfonyl methane. About 5.6% to 26% TRR extractable residues remained unidentified, while 7.4% to 77% TRR residues in remaining solids were uncharacterized.

No appreciable amount of parent compound was found in any following crops grown in soil 1 month after treatment (see Table 19). Ethylsulfonyl methylsulfonyl methane was the predominant metabolite in the crops, most likely arising from hydrolysis of phorate sulfone. Other metabolites identified were phorate sulfoxide, phorate sulfone, and phoratoxon sulfoxide. About 34% to 85% TRR extractable residues remained unidentified, while 3.9%–22% TRR residues in remaining solids were uncharacterized.

Very low levels of residues (< 0.01 mg/kg eq) were found in follow crops grown in the soil 3 and 12 months after treatment. Therefore, it was not possible to extract and characterise these low level radioactive residues in the crops.

Table 18. Distribution of residues in extracts of soil.

Soil depth (cm)	Sampling interval [months]	TRR mg/kg eq	MeOH /H_2O %TRR	Solids %TRR	Distribution of metabolites in MeOH/H_2O extracts %TRR [a]							
					parent	P-SO	P-SO2	PO	PO-SO	PO-SO2	M1	Unk
0-7.6	0	0.55	-	-	-	-	-		-	-	-	
0-7.6	0.5	1.2	-	-	-	-	-		-	-	-	
7.6-15	0.5	< 0.01	-	-	-	-	-		-	-	-	
0-7.6	1	1.1	93%	7.4%	0.19%	0.0%	66%	-	0.0%	0.0%	0.0%	26%
		(b)	82%	18%	1.3%	11%	63%	0.16%	0.20%	0.63%	0.0%	5.6%
7.6-15	1	0.03										
0-7.6	3	0.28	36%	64%	0.54%	0.98%	27%	-	0.0%	-	0.18%	7.2%
7.6-15	3	0.02										
0-7.6	12	0.18	23%	77%	0.0%	0.43%	6.7%	-	0.0%	-	0.29%	16%
7.6-15	12	0.01	-	-	-	-	-		-	-	-	
15-23	12	< 0.01	-	-	-	-	-		-	-	-	
23-30	12	< 0.01	-	-	-	-	-		-	-	-	

- not investigated/analysed
imm = immature; mat = mature

P-SO = phorate sulfoxide, P-SO2 = phorate sulfone,
PO= phoratoxon; PO-SO = phoratoxon sulfoxide, PO-SO2 = phoratoxonsulfone
M1 = ethylsulfonyl methylsulfonyl methane,
unk = unknown compounds, representing 3-4 different compounds at 0.11% TRR to 15% TRR each.
a %TRR calculated by the present reviewer from %extractable radioactivity.
b this sample was analysed twice: once in report PA-730-001 and once in report PA-730-002. In report PA-730-002 reference standard for phoratoxon was included.

Table 19. Distribution of residues in extracts of rotational crops.

Commodity	Planting interval	Harvest interval	TRR mg/kg eq	MeOH / H_2O %TRR	Solids %TRR	Distribution of metabolites in MeOH/H_2O extracts %TRR [a]					
						parent	P-SO	P-SO2	PO-SO	M1	Unk
imm maize plant	1 m	1 m	0.72	91%	8.7%	2.2%	3.2%	3.5%	3.6%	41%	38%
imm maize plant	1 m	2 m	0.39	93%	6.6%	0.0%	0.0%	0.0%	0.0%	16%	78%
mat maize kernel	1 m	4 m	0.03	-	-	-	-	-	-	-	-
mat maize cob	1 m	4 m	0.02	-	-	-	-	-	-	-	-
mat maize fodder	1 m	4 m	0.32	69%	31%	0.0%	0.0%	0.0%	0.0%	0.0%	100%
imm lettuce	1 m	1.5 m	1.4	93%	6.7%	0.0%	2.5%	1.0%	0.0%	54%	35%
mat lettuce	1 m	2.0 m	0.47	79%	21%	0.0%	1.5%	0.09%	0.0%	19%	59%
imm beet leaf	1 m	1.5 m	1.7	96%	3.9%	3.8%	0.0%	0.74%	0.0%	57%	34%
imm beet tuber	1 m	1.5 m	0.69	85%	15%	0.0%	0.0%	0.0%	0.0%	0.0%	85%
mat beet leaf	1 m	2.0 m	0.75	94%	5.5%	0.0%	1.3%	0.60%	0.0%	51%	42%
mat beet tuber	1 m	2.0 m	0.53	78%	22%	0.0%	0.0%	0.0%	0.0%	3.7%	75%
imm wheat plant	31 d	40 d	0.40	81%	19%	0.0%	0.0%	0.0%	0.0%	16%	65%
mat wheat straw	31 d	97 d	0.24	56%	44%	0.0%	0.0%	0.0%	0.0%	7.8%	48%
mat wheat grain	31 d	97 d	0.17	49%	51%	-	-	-	-	-	-
imm maize plant	3 m	1 m	0.09	84%	16%	-	-	-	-	-	-
imm maize kernel	3 m	3 m	< 0.01	-	-	-	-	-	-	-	-
imm maize cob	3 m	3 m	< 0.01	-	-	-	-	-	-	-	-
imm maize fodder	3 m	3 m	0.03	-	-	-	-	-	-	-	-
mat maize kernel	3 m	4 m	< 0.01	-	-	-	-	-	-	-	-
mat maize cob	3 m	4 m	< 0.01	-	-	-	-	-	-	-	-
mat maize fodder	3 m	4 m	0.02	-	-	-	-	-	-	-	-
mat lettuce	3 m	2.5 m	0.03	-	-	-	-	-	-	-	-
mat radish leaf	3 m	1 m	0.06	-	-	-	-	-	-	-	-
mat radish tuber	3 m	1 m	0.03	-	-	-	-	-	-	-	-
imm wheat plant	91 d	58 d	0.22	85%	15%	-	-	-	-	-	-
mat wheat straw	92 d	122 d	0.06	-	-	-	-	-	-	-	-
mat wheat grain	92 d	122 d	-	-	-	-	-	-	-	-	-
imm maize plant	12 m	1.5 m	0.01	-	-	-	-	-	-	-	-
mat maize kernel	12 m	4.0 m	< 0.01	-	-	-	-	-	-	-	-
mat maize cob	12 m	4.0 m	< 0.01	-	-	-	-	-	-	-	-
mat maize fodder	12 m	4.0 m	< 0.01	-	-	-	-	-	-	-	-
mat lettuce	12 m	1.5 m	0.03	-	-	-	-	-	-	-	-
mat radish leaf	12 m	1.5 m	0.05	-	-	-	-	-	-	-	-
mat radish tuber	12 m	1.5 m	0.02	-	-	-	-	-	-	-	-
imm wheat plant	377	54	0.07	-	-	-	-	-	-	-	-
mat wheat straw	452	106	0.05	-	-	-	-	-	-	-	-
mat wheat grain	452	106	0.02	-	-	-	-	-	-	-	-

planting interval = period between treatment of soil and planting/seeding of the crop: m = months
harvest interval = period between planting/seeding of the crop and harvest of the crop: m = months
- not investigated/analysed

imm = immature; mat = mature
P-SO = phorate sulfoxide, P-SO2 = phorate sulfone, PO-SO = phoratoxon sulfoxide,
M1 = ethylsulfonyl methylsulfonyl methane,
unk = unknown compounds, representing 3-10 different compounds at 0.25% TRR to 100% TRR each.
a %TRR calculated by the present reviewer from %extractable radioactivity.

Study 3. Another confined accumulation study was conducted in the USA in 1990-1992, where the uptake of residues of phorate were determined in rotational crops grown in aged soil treated with ^{14}C-phorate at the rate of 3.8 kg ai/ha (Brindle, 1992: PA-640-003). The plot was located outdoors in Madera, California, USA. On the day before application, the top 5 cm of surface soil were removed and the entire plot dampened with water. Soil characteristics were sandy loam, pH 6.2, 0.5% om, 9.5% clay. Phorate, ^{14}C labelled at the methylene position, was applied using a CO_2 pressurised backpack sprayer. The radiolabel with > 96% radiopurity had a specific activity of 40 mCi/g for the undiluted substance and 5.2 mCi/g for the diluted substance. Following the application, the soil removed was replaced over the treated area, simulating field use incorporation of the commercial granular formulation of phorate. Nine months and 12 months after treatment carrots (Imperator), lettuce (Waldmann Greenleaf), peas (HP 679-1-6-1), and barley (NK-BB82-2) were planted on the treated plots. Soil and crops were harvested at various intervals. Soil was sampled as 45 cm cores, which were divided in 15 cm sections. Carrot samples were separated into roots and green leaves plus tops. Carrot roots were rinsed with water to remove soil particles. Green pea samples were separated in pea vines, pods and seeds. Dry pea samples were separated in dry seeds and dry pea vines plus pods. Mature barley samples were separated into straw and heads. The heads were threshed to separate grain from chaff. The chaff was added to the straw samples. All samples were blended and were kept at -20°C for 7 to 43 days.

Total radioactive residues in crops, extracts and solids were determined by (combustion) LSC. Soil and crops were extracted with MeOH:water solution (9:1, v/v for soil, 4:1, v/v for crops). Extracts were fractionated and identified by 2D-TLC (6 systems) against reference standards. Reference compounds used were parent, phorate sulfoxide, phorate sulfone, phoratoxon, phoratoxon sulfoxide, phoratoxon sulfone, ethylsulfonyl methylsulfonyl methane, ethyl (methyl-sulfinyl)methyl sulfone, and (ethylsulfinyl)methyl methyl sulfone. Major bands from TLC were isolated, cleaned up and isolated by HPLC (2 systems) for confirmatory identification (2D-TLC and/or GC-MS or GC-FPD).

Table 20 summarises the TRR distribution in soil treated with ^{14}C-phorate. The total radioactive residue (TRR 1.05 to 1.55 mg/kg eq) from 0-DAT (soil 0 - 15 cm) contained about 95%-97% TRR parent. In soil at 9 MAT (TRR 0.17 mg/kg eq), 41% TRR was extractable. No parent compound was detectable and the principal component was phorate sulfone (39% TRR). Solids remaining after MeOH/water extraction could be released by acid (24% TRR) and base extraction (22%), while 13% TRR was not extractable. Acid extraction released several polar components which were all less than 0.01 mg/kg eq. In the basic extract, 3.5% TRR was related to the humic acid fraction. In soil at 12 MAT, phorate sulfone was detectable only as a trace amount. Instead, a fraction containing very polar components, as characterised by HPLC, mostly comprised the organosoluble residue of soil.

Table 21 summarises the TRR in plants grown in soil treated with ^{14}C-phorate. Dried plant tissue taken at harvest contained higher residues than the corresponding green, mid-harvest samples. The extractability of the TRR from the different crop samples with MeOH/water solution was very variable. The extremes were lettuce (harvest sample, 9 MAT), which yielded 93% TRR compared to dry pea seeds (9 MAT) which yielded only 41% TRR. The parent compound was not detectable in any of the crop samples. The only phosphorylated residue identified in significant amount was phorate sulfone and this was present only in crops from the 9 MAT plot. At harvest, only trace quantities of phorate sulfone were observed only in carrot roots. A predominant component of the organosoluble crop residue from both planting intervals was the ethylsulfonyl methylsulfonyl methane. In the 12 MAT samples, ethylsulfonyl methylsulfonyl methane was essentially the only component present in the organosoluble residue. Phorate sulfoxide and phoratoxon were not found in any of the crop samples.

The remaining radioactivity (unknowns in Table 21) was attributable to very polar, water-soluble ^{14}C-components as characterized by TLC and HPLC. These components did not partition into methyl isobutyl ketone, were unaffected by β-glucosidase or sulfatase (each 4 hrs at 37 °C), but did show potential for silylation, indicating the presence of free hydroxyl groups.

The solids fraction was characterized further. Starch was isolated from homogenised barley grain by DMSO extraction for 18 hrs. After centrifugation, EtOH was added to the supernatant to precipitate the starch. The starch was dried at 60 °C. Dried starch was acid-hydrolysed to glucose with 0.1 M HCl for 4 hrs on a steam bath and filtered. Phenylhydrazine, HCl and sodium acetate were added to the filtrate and left for 3 hr on a steam bath. The glucozanone precipitate was collected by centrifugation and was cleaned-up. Protein was isolated from homogenised dry pea seeds by soaking with 10% NaCl overnight. After centrifugation, the supernatant was saturated with ammonium sulfate. After standing overnight at 4°C, the precipitated protein was collected by ultracentrifugation. Cellulose and lignin were isolated from the solids remaining after MeOH/water extractions. The solids were re-extracted with 2% HCl in MeOH/water (4:1) and the solids were collected. For pea seeds from protein isolation, the solids remaining after 10% NaCl extraction were re-extracted with MeOH/water (4:1) and the solids were collected. Solids were refluxed for 18 hrs with 10% NaOH and filtered. The remaining filter cake is the cellulose fraction. The filtrate was acidified to pH 1.0 with concentrated HCl and left for 4 hrs. The lignin precipitate was collected by centrifugation.

The non-extractable portion of the TRR (solids in Table 21) was shown to be associated with a variety of endogenous cell components. Isolated starch from barley grain, isolated protein from peas, and isolated cellulose and lignin from barley straw, carrot roots, peas and pea vines were all shown to be significantly radiolabelled (see Table 22). Radioactivity was characterised in natural compounds to the level of ^{14}C-glucose. This was achieved by acid-hydrolysis of the isolated barley grain starch, followed by formation and purification of a ^{14}C-glucosazone derivative. The labelling of endogenous glucose was unequivocal evidence that single carbon units derived from phorate residues were part of a metabolic carbon pool which provided precursors for the biosynthesis of the structural and storage components such as cellulose, lignin and protein.

Table 20. Total radioactive residues in soil samples from plots treated with ^{14}C-phorate.

	9 month planting interval		12 month planting interval	
Soil core samples (0-15 cm)	Range mg/kg eq	Average mg/kg eq	Range mg/kg eq	Average mg/kg eq
0-DAT	0.19 – 1.2	1.0	1.2 – 1.6	1.4
Crop planting	0.10 – 0.17	0.14	0.07 – 0.08	0.08
Mid-harvest	0.07 – 0.19	0.11	0.03 – 0.14	0.07
Final harvest	0.07 – 0.25	0.13	0.02 – 0.10	0.06

Table 21. Distribution of residues in extracts of rotational crops.

Sample	Planting interval d	Harvest interval d	TRR mg/kg eq	Extract %TRR	Solids %TRR	Distribution of metabolites in MeOH/H_2O extracts %TRR [a]					
						P-SO2	PO-SO	PO-SO2	M1	M2/3	Unk
carrot roots	274	69 mid	0.16	81%	19%	25%	0.0%	0.0%	0.0%	0.0%	50%
carrot leafs	274	69 mid	0.96	88%	12%	0.0%	0.0%	0.0%	38%	7.3%	38%
lettuce	274	39 mid	0.47	72%	28%	4.3%	0.0%	4.3%	13%	4.3%	47%
pea seeds	274	53 mid	0.57	63%	37%	1.8%	0.0%	1.8%	7.0%	3.5%	47%
pea pods	274	53 mid	0.69	54%	46%	1.4%	0.0%	1.4%	17%	4.3%	29%
pea vines	274	53 mid	1.80	61%	39%	0.0%	0.0%	0.0%	30%	2.8%	25%

Sample	Planting interval d	Harvest interval d	TRR mg/kg eq	Extract %TRR	Solids %TRR	Distribution of metabolites in MeOH/H_2O extracts %TRR [a]					
						P-SO2	PO-SO	PO-SO2	M1	M2/3	Unk
barley plant	274	39 mid	1.90	87%	13%	16%	0.0%	0.0%	12%	4.7%	53%
carrot roots	274	124 final	0.13	77%	23%	7.7%	0.0%	0.0%	7.7%	0.0%	62%
carrot leafs	274	124 final	0.79	89%	11%	0.0%	0.0%	0.0%	41%	1.3%	43%
lettuce	274	63 final	0.48	94%	6.2%	0.0%	0.0%	0.0%	56%	8.3%	23%
pea seeds	274	81 final	2.62	41%	59%	0.0%	0.0%	0.0%	12%	1.5%	25%
pea vines	274	81 final	10.54	62%	38%	0.28%	0.38%	0.28%	27%	1.4%	33%
barley grain	274	89 final	0.89	60%	40%	0.0%	0.0%	0.0%	15%	3.4%	40%
barley straw	274	89 final	4.45	89%	11%	0.0%	0.0%	0.0%	28%	4.0%	56%
carrot roots	365	181 mid	0.01	80%	20%	0.0%	0.0%	0.0%	0.0%	0.0%	0.0%
carrot leafs	365	181 mid	0.03	87%	13%	0.0%	0.0%	0.0%	0.0%	0.0%	0.0%
lettuce	365	81 mid	0.19	95%	5.3%	0.0%	0.0%	0.0%	47%	5.3%	21%
pea seeds	365	181 mid	0.03	67%	33%	0.0%	0.0%	0.0%	0.0%	0.0%	0.0%
pea pods	365	181 mid	0.03	100%	0.0%	0.0%	0.0%	0.0%	0.0%	0.0%	0.0%
pea vines	365	181 mid	0.19	90%	10%	0.0%	0.0%	0.0%	16%	0.0%	68%
barley plant	365	81 mid	0.21	95%	4.8%	0.0%	0.0%	0.0%	48%	0.0%	24%
carrot roots	365	221 final	< 0.01	-	-	-	-	-	-	-	-
carrot leafs	365	221 final	0.08	88%	12%	0.0%	0.0%	0.0%	63%	0.0%	25%
lettuce	365	156 final	0.04	75%	25%	0.0%	0.0%	0.0%	50%	0.0%	0%
pea seeds	365	209 final	0.24	62%	38%	0.0%	0.0%	0.0%	25%	0.0%	33%
pea vines	365	209 final	2.31	85%	15%	0.0%	0.0%	0.0%	29%	0.0%	52%
barley grain	365	221 final	0.04	50%	50%	0.0%	0.0%	0.0%	trace	0.0%	25%
barley straw	365	221 final	0.25	80%	20%	0.0%	0.0%	0.0%	48%	0.0%	20%

planting interval = period between treatment of soil and planting/seeding of the crop
harvest interval = period between planting/seeding of the crop and harvest of the crop
- not investigated/analysed
P-SO2 = phorate sulfone, PO-SO = phoratoxon sulfoxide, PO-SO2 = phoratoxon sulfone
M1 = ethylsulfonyl methylsulfonyl methane,
M2/3 = ethyl (methylsulfinyl)methyl sulfone and/or (ethylsulfinyl)methyl methyl sulfone,
unk = unknown compounds remaining at the origin of TLC and characterized as polar metabolites.
a %TRR calculated by the present reviewer from mg/kg eq values in extracts

Table 22. Characterization of solids from rotational crops.

Crop	Planting interval d	Harvest interval d	TRR mg/kg eq	Solids	Characterization of solids [a]
carrot roots	274	69 mid	0.16	19%	3.2% TRR cellulose 1.5% TRR lignin 10% TRR post-lignin acidified supernatant
barley grain	274	89 final	0.89	40%	27% TRR starch 10% TRR insoluble fiber and protein
barley straw	274	89 final	4.45	11%	0.64% TRR cellulose 1.0% TRR lignin 9.2% TRR post-lignin acidified supernatant
pea vines	274	81 final	10.54	38%	7.6% TRR cellulose 4.7% TRR lignin 21% TRR post-lignin acidified supernatant
pea seeds	365	209 final	0.24	38%	8.4% TRR protein 6.3% TRR cellulose 6.4% TRR lignin 20% TRR post-lignin acidified supernatant

a For the characterization of solution, new samples were used and slightly different extraction procedures were followed. This means that %TRR in original solids fraction can differ from sum of %TRR values after characterization of solids.

Study 4. A separate confined accumulation study was conducted in the USA in 1994 specifically to determine the total residues in crops (barley, carrots, lettuce and peas) grown in soil four months after treatment with ^{14}C-phorate at rates of 3.8 kg ai/ha (Brindle, 1993: PA-640-004). In addition the potential for barley to take up phorate related residues from soil was studied at an application rate of 1.46 kg ai/ha. The same protocol as in study 3 was followed. Differences with study 3 were: a) the specific activity for the diluted substance was slightly lower (4.9 mCi/g), b) the soil characteristics were sandy loam, pH=6.4, 0.7% om, 6.7% clay; c) crop varieties were barley (BB82-425), peas (HP-679-1-6-1), lettuce (Waldman) and carrots (Imperator 58); d) blended samples were kept at -20°C for 12 to 43 d; e) reference compounds used were parent, phorate sulfoxide, phorate sulfone, phoratoxon sulfone; ethylsulfonyl methylsulfonyl methane; sulfone, ethyl (methyl-sulfinyl)methyl sulfone, and (ethylsulfinyl)methyl methyl sulfone.

The TRR from soil (0-15 cm depth) are shown in Table 23. At 0-DAT, the entire residue was extractable and the residue consisted predominantly of phorate (87% TRR) with a small amount of phorate sulfone (6–7% TRR). At 24 DAT, 67%–88% TRR was extractable; the extractable residue consisted predominantly of phorate sulfone (85% TER) with 7% TER as unknown polar material. At crop planting, 6.1%–46% TRR was extractable; the phorate sulfone had decreased to 11%–20% TER, while 16%–17% TER was identified as ethylsulfonyl methylsulfonyl methane, and 39%–52% TER was polar material.

TRR in rotational crops were low for the harvest commodities (0.03 – 0.05 mg/kg eq). Dried pea seeds, dried pea vines and barley straw contained slightly higher TRR (0.10 – 0.22 mg/kg eq). Table 24 summarises the results. Neither phorate (parent) nor any phosphorylated metabolites of phorate were found in any of the mid-harvest and harvest crops. The extractable residue from all crop samples consisted of 9.1%–28% TRR ethylsulfonyl methylsulfonyl methane and very polar, water-soluble ^{14}C-components as characterized by TLC and HPLC. The non-extractable portion of the TRR was shown to be naturally occurring endogenous components by the significant incorporation of ^{14}C-phorate into protein isolated from dry pea seeds and cellulose and lignin from dry pea vine (Table 25).

Table 23. Total radioactive residues in soil samples from plots treated with ^{14}C-phorate.

Soil core samples (0-15 cm)	3.8 kg ai/ha range mg/kg eq	1.5 kg ai/ha range mg/kg eq
0-DAT	0.84-0.96	0.53-0.54
24-DAT	0.55-1.23	0.37-0.68
Crop planting	0.14-1.02	0.09-0.14
Mid-harvest	0.07-0.20	0.05-0.10
Final harvest	0.07-0.15	0.06-0.11

Table 24. Distribution of residues in extracts of rotational crops, planted 4 months after soil treatment.

Sample	stage	DAT	TRR mg/kg eq	Extract %TRR (a)	Solids %TRR (a)	M1 (a)
carrot roots	mid	329	0.04	85	15	nd
carrot leafs	mid	329	0.11	83	17	9.1
lettuce	mid	167	0.17	89	11	24
pea seeds	mid	266	0.07	-	-	-
	mid	305	0.02	70	30	-
pea pods	mid	266	0.05	84	16	nd
	mid	305	0.02	70	30	-
pea vines	mid	266	0.18	84	16	28

Sample	stage	DAT	TRR mg/kg eq	Extract %TRR (a)	Solids %TRR (a)	M1 (a)
	mid	305	0.08	80	20	-
barley plant	mid	167	0.39	89	11	nd
barley plant	mid	167	0.33	92	7.9	-
carrot roots	final	369	0.04	80	20	nd
carrot leafs	final	369	0.04	78	22	25
lettuce	final	266	0.05	84	16	20
pea seeds	final	369	0.15	27	73	nd
pea vines	final	369	0.22	22	78	nd
barley grain	final	370	0.05	12	88	nd
barley straw	final	370	0.10	53	47	nd
barley grain	final	370	0.03	-	-	-
barley straw	final	370	0.04	-	-	-

-	not investigated/analysed
nd	not detected (< 0.01 mg/kg eq)
M1	ethylsulfonyl methylsulfonyl methane
a	%TRR calculated by the present reviewer from mg/kg eq values in extracts

Table 25. Characterization of solids from rotational crops.

Crop	stage	DAT	TRR mg/kg eq	Solids %TRR	Characterization of solids (a)
pea vines	final	369	0.22	78	5.6% extractable with 2% HCl in MeOH/water 16% TRR cellulose 9.7% TRR lignin 43% TRR post-lignin acidified supernatant
pea seeds	final	369	0.15	73	23% TRR protein 7.6% TRR cellulose 9.9% TRR lignin 20% TRR post-lignin acidified supernatant

a For the characterization of solids, new samples were used and slightly different extraction procedures were followed. This means that %TRR in original solids fraction can differ from sum of %TRR values after characterization of solids.

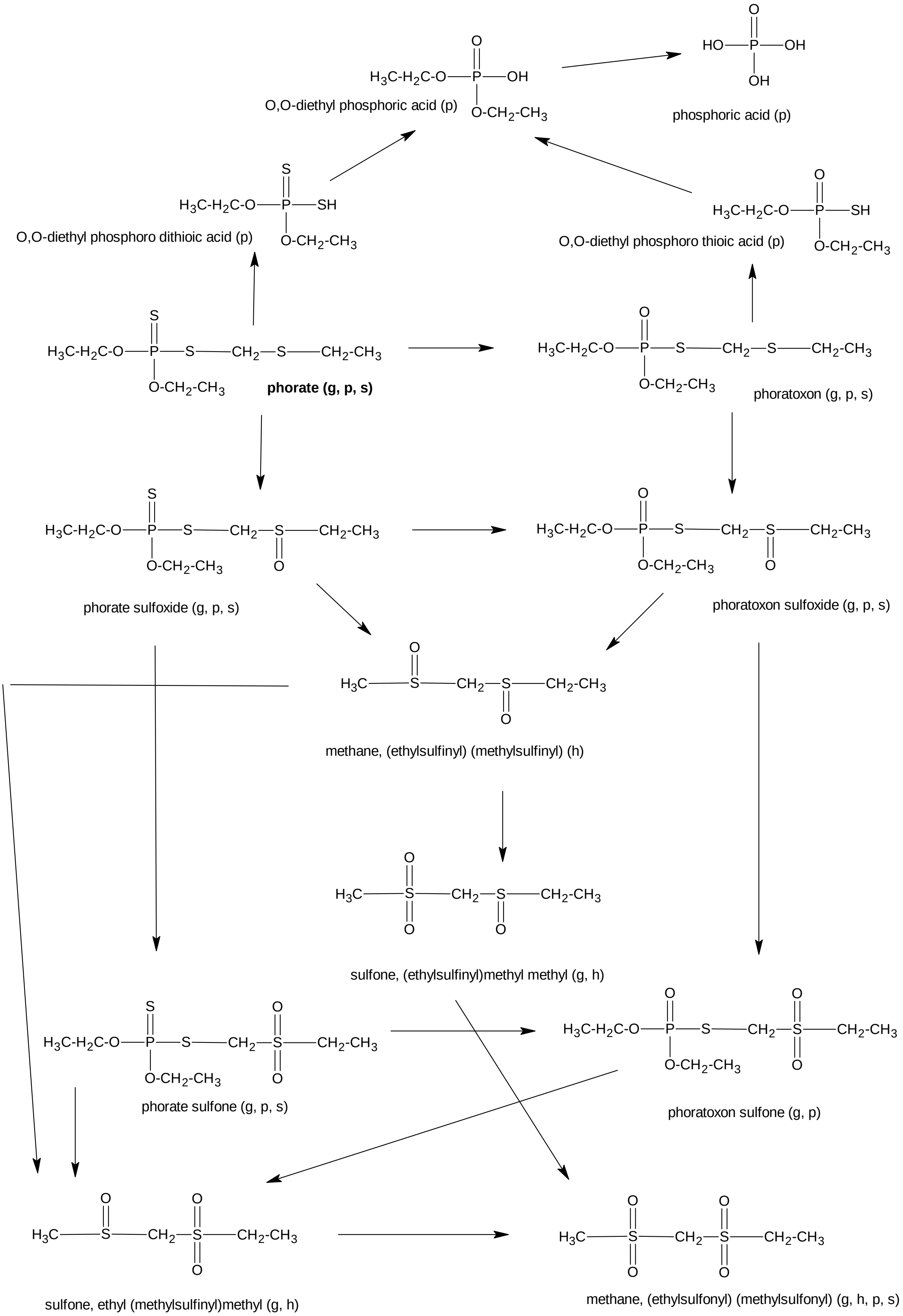


Figure 2 Metabolism of phorate in goats (g), hens (h), and plants (p) and degradation in aerobic soil (s)

Environmental fate in water/sediment systems

Phorate is metabolized in soil to form the oxidized compounds, phorate sulfoxide and phorate sulfone. The Meeting received information on the hydrolysis of these three compounds in water.

Hydrolysis in water

The hydrolysis of ^{14}C-phorate, ^{14}C-phorate sulfoxide, and ^{14}C-phorate sulfone in sterile buffer systems was investigated under laboratory conditions (Martin and Heim, 1999: PA-630-005). Each compound was labelled at the carbon atom positioned between the two sulfur atoms (^{14}C methylene position). The radiochemical purities were 95.0%-99.9%, specific activities were 28.99-37.84 mCi/g and chemical purities were 81.0%-99.3%. The actual test substance concentrations at initiation were 0.882 to 1.15 mg/L. Solutions at pH 5, 7, and 9 were prepared as 0.05 M sodium acetate buffer, 0.05 M potassium/sodium phosphate buffer or 0.05 M potassium/sodium borate buffer, respectively. The study was performed in duplicate using flow-through test systems where CO_2-free air was continuously pulled through the headspace of the flasks by a vacuum pump and the volatiles from the flasks were passed through one Orbo-25 tube, two ethylene glycol traps, two foam plugs, and two 1N KOH traps arranged in series. The flasks were incubated in the dark in temperature-controlled environmental chambers at different temperatures and different pH-values (see Table 26). Total incubation period (3-56 d) and sampling times were based on half-life estimates. Samples were taken at a minimum of ten intervals defined for each temperature, pH, and test substance.

Samples were stored frozen (temperature not stated) for 157 d for ^{14}C-phorate and 191 d for ^{14}C-phorate sulfoxide and ^{14}C-phorate sulfone. Storage stability was evaluated by HPLC analysis of day 0 buffer solutions after freezer storage. Recovery was 100% for all three compounds.

LSC was used to determine the total ^{14}C-activity in buffer solutions at each sample point. The ^{14}C-test substances and the ^{14}C-degradation products of their hydrolysis were quantified by HPLC with ^{14}C flow-through and UV detector. The test substances were characterised by matching the observed retention time with the respective reference standards: phorate, phorate sulfoxide, phorate sulfone, phorate oxon, phorate oxon sulfoxide, phorate oxon sulfone, ^{14}C-paraformaldehyde, and ^{14}C-formaldehyde. Characterisation of unknown degradates was performed by HPLC-MS and derivatization using 2,4-dinitrophenylhydrazine (DNPH). TLC was used only as a qualitative confirmatory method.

Radioactivity in buffer solutions declined with time coinciding with the appearance of ^{14}C-volatiles. Total radioactive recoveries at test termination ranged from 96% to 108% TAR. Small amounts of volatile radioactivity was recovered from the Orbo tubes (<5% TAR), ethylene glycol traps (<3% TAR), foam plugs (< 0.02% TAR), and KOH traps (< 1.2% TAR). Mass balance was less than 90% at intermediate sampling points in some ^{14}C-phorate test systems. This was due to volatile radioactivity being absorbed by the Tygon tubing in the test system: up to 32 % TAR was extracted from the tubing at test termination in the phorate test systems. HPLC analyses of the extracts showed that this material was phorate.

The first-order rate constant, k, for hydrolysis was determined for each test system replicate by linear regression of a plot of the natural log of the concentration of test substance versus time. The half-life (DT_{50}) and DT_{90} were calculated, and the average values are summarized in Table 26. The DT_{50} values for the phorate test systems included a contribution due to volatilisation; however, hydrolysis was rapid even when volatilisation was taken into account. The Arrhenius equation was used to estimate the DT_{50} values at 25°C.

Table 26. Calculated DT_{50} and DT_{90} for phorate, phorate sulfoxide, and phorate sulfone.

	Phorate			Phorate sulfoxide			Phorate sulfone		
pH	Temp. (°C)	Mean DT_{50} (d)	Mean DT_{90} (d)	Temp. (°C)	Mean DT_{50} (d)	Mean DT_{90} (d)	Temp. (°C)	Mean DT_{50} (d)	Mean DT_{90} (d)
5	10	14.8	49.2	40	27.8	92.3	40	13.5	44.7
	20	5.54	18.4	50	10.1	33.4	50	5.1S	17.1
	30	1.16	3.83	60	3.03	10.0	60	1.74	5.78
7	10	18.2	60.5	40	19.5	64.7	40	9.80	32.6
	20	5.20	17.3	50	6.79	22.6	50	3.54	11.8
	30	1.25	4.16	60	2.31	7.66	60	1.16	3.85
9	10	20.5	68.1	20	14.2	47.0	20	10.8	35.8
	20	5.30	17.6	30	3.28	10.9	30	2.53	8.40
	30	0.920	3.05	40	1.31	4.36	40	0.811	2.70

Phorate hydrolyses rapidly under abiotic conditions. The rate of hydrolysis of phorate increased significantly as temperature increased at all three pH levels tested. The effect of pH on hydrolysis rate was not significant. The major degradate (max 31%-87% TAR at termination) observed in all treatments was formaldehyde, which was identified by derivatization with 2, 4-dinitrophenylhydrazine. Phorate sulfoxide (max 5.2%-6.6% TAR at day 1) was formed only at pH 5. The hydrolysis half-lives at 25°C were estimated to be 2.36, 2.47, and 2.08 d, for pH 5, 7, and 9, respectively. The results show that phorate will degrade under abiotic conditions and will not be expected to persist in aquatic systems.

Hydrolysis of phorate sulfoxide occurs more slowly. The rate of hydrolysis increased significantly as temperature increased at all three pH levels tested and as pH increased at each temperature. A major degradate formed only at pH 5-7 was desethyl phorate sulfoxide (max 37%-72% TAR at termination), which was identified by HPLC-MS. Formaldehyde was identified as another major degradate observed mainly at pH 9 (max 68%-84% TAR at termination) and to a lesser extent at pH 5-7 (max 15%-36% TAR at termination). An unidentified degradate was formed only at pH 9, reaching a maximum of 11% TAR in the 30°C test systems at day 4 and declining to <2.1 % TAR by termination at day 14. Attempts to identify this degradate by HPLC-MS and NMR were unsuccessful. At 25°C, hydrolysis half-lives were estimated to be 185, 118, and 7.02 d at pH 5, 7, and 9, respectively. The degradation pathway of phorate sulfoxide was pH-dependent at elevated temperatures with de-esterification being the predominant reaction at pH 5-7.

Hydrolysis of phorate sulfone occurs more slowly. The rate of hydrolysis increased significantly as temperature increased at all three pH levels tested and as pH increased at each temperature. A major degradate formed only at pH 5-7 was desethyl phorate sulfone (max 27%-62% TAR at termination), which was identified by HPLC-MS. Formaldehyde was identified as another major degradate observed mainly at pH 9 (88%-96% TAR at termination) and to a lesser extent at pH 5-7 (max 19%-46% TAR at termination). At 25°C, hydrolysis half-lives were estimated to be 77.1, 60.2, and 5.25 d at pH 5, 7, and 9, respectively. The degradation pathway of phorate sulfone was pH-dependent at elevated temperatures with de-esterification being the predominant reaction at pH 5-7.

METHODS OF RESIDUE ANALYSIS

The meeting received information on methods of residue analysis for enforcement and residue methods used in the various study reports.

Enforcement methods

The Pesticide Analytical Manual (PAM) Volume II lists ten methods (Method I and A-L, 1963-1973) for the enforcement of MRLs for phorate residues in/on plants and animal commodities. The description of method I, IA, IB was submitted. Method I is based on the extraction of the parent and its oxygenated metabolites phorate sulfoxide, phorate sulfone, phoratoxon, phoratoxon sulfoxide and phoratoxon sulfone. The extracts are cleaned-up by liquid-liquid partitioning or alumina column chromatography. Phorate-related residues are oxidized to the common moiety metabolite, phoratoxon sulfone, using 3-chloroperoxybenzoic acid. The oxidized product is then analyzed by GC with a phosphorus specific detector.

Method I is validated for animal commodities (milk, meat, fat, meat byproducts). Milk, meat and meat byproducts are extracted with chloroform, fat is extracted with acetonitrile. The oxidation of phorate to phoratoxon sulfone is about 70% complete. Because of this, parent recoveries are based on oxidized phorate, while phoratoxon sulfone recoveries are based on phoratoxon standards. Recoveries from milk samples resulted in 75%-85% for the parent compound at 0.02 mg/kg eq and 95%-103% for phoratoxon sulfone at 0.04 mg/kg eq. The reported LOQ was 0.01 mg/kg eq for milk and 0.02 mg/kg eq for meat tissues (cattle, goat, hogs, horses, and sheep).

Method IA is validated for cottonseed and safflower seed. Samples are extracted with 10% methanol in chloroform. Validation results are not available.

Method IB is validated for sugarbeets with a reported LOQ of 0.1 mg/kg eq. Samples are extracted with chloroform. Final analysis is by TLC with IR detection. This method is considered an identification method in case a confirmatory analysis is required.

Phorate and its five metabolites (Phorate, phorate sulfoxide, phorate sulfone, phoratoxon, phoratoxon sulfoxide, and phoratoxon sulfone) were taken through the USA FDA multiresidue method protocols described in PAM Volume I with some success (Gross, 1990: PA-244-034).

Protocol A/B: Phorate and its five metabolites were not tested through protocols A and B since they do not contain an N-methylcarbamate structure and they are not an acid or a phenol.

Protocol C: GC-characteristics. All six compounds gave adequate responses and good peaks with the flame photometric detector and the four recommended GC-columns. For the electron capture detector, higher injection amounts were needed for these compounds to give peaks of 50% full scale deflection.

Protocol D: Non-fatty foods only. All six compounds are adequately recovered using multiresidue method section 302 (Luke method, DEGS column). Using sugarbeet roots fortified in duplicate at levels of 0.1 and 0.3 mg/kg for each compound individually, individual recoveries ranged from 78%-144%. No interferences were observed in a control sample or a reagent blank.

Protocol E: Of the six compounds, only phorate and phorate sulfone were recovered through the Florisil clean-up column. Using sugarbeet roots fortified in duplicate at 0.05 and 0.30 mg/kg and maize grain fortified in duplicate at 0.05 and 0.10 mg/kg for each compound individually, individual recoveries of phorate were good with values between 72%-107%, while those of phorate sulfone were unsatisfactory with values between 12%-38%.

Analytical methods used in study reports

Acetylcholinesterase essays in plant and animal commodities

Residues in very early studies (1961-1963) were analysed by their acetylcholinesterase inhibitive power in an electrometric acetylcholinesterase essay.

Method A was used in 1962 and 1963 residue trials on cottonseed. A full method description was available in Zaki and El-Sayed, 1968 (PA-905-048). Crop samples were extracted with water. In the 1963 study, residues were partitioned between water-chloroform and both layers were analysed. The pH of the extracts was adjusted to 7.8. Horse plasma (as acetylcholinesterase source) was added and the mixture was incubated for 70 min at 37 °C. An aliquot was mixed with barbital-phosphate buffer and left for 10 min at 37 °C. Acetylcholine chloride solution was added and left for 120 min at 37 °C. The difference in pH before and after acetylcholine addition is a measure for acetylcholinesterase power of the tested extracts. Total phorate-related residues were calculated from standard calibration curves for oxidized phorate. No method validation report is available.

The essay is non-specific and there is no correlation between total phorate-related residue concentration and acetylcholinesterase activity. Residues with higher acetylcholinesterase activity than oxidized phorate, will give an erroneously high residue concentration, whereas compounds with lower acetylcholinesterase activity than oxidized phorate will give an erroneously low residue concentration.

Method B was used in 1961 feeding studies in calves and dairy cattle. A full method description and validation report is available in Hill, 1961 (PA-705-009). Animal tissues (liver, kidney, muscle, milk) were extracted with chloroform; fat was extracted with ACN. Liver, kidney, muscle extracts were cleaned-up by hexane-ACN partitioning. Milk and fat extracts were cleaned-up on a polyethylene-coated alumina column with water-ACN as eluant. Each of the cleaned-up tissue extracts (liver, kidney, muscle, milk, fat) was further cleaned up by water-chloroform partitioning. Phorate-related residues in the chloroform extract were oxidized with peracetic acid to phoratoxon sulfone. The reaction mixture is cleaned-up by water-benzene partitioning. The benzene extract was evaporated to dryness and redissolved in acetone. Water and human blood plasma (as acetylcholinesterase source) were added and the mixture was incubated for 60 min at 37°C. An aliquot was mixed with acetylcholine bromide solution in barbital-phosphate buffer (pH 8.0) and left for 120 min at 37°C. The difference in pH before and after acetylcholine addition is a measure for acetylcholinesterase power of the tested extracts. Total phorate-related residues (oxidizable to phoratoxon sulfone) were calculated from standard calibration curves for oxidized phorate.

Method B has been validated on animal commodities using a limited number of recovery samples per concentration level (n <5), a limited number of compounds which was used for recovery checks (phorate and 5 oxidized metabolites), and a limited number of control samples analysed (n <2) (see Table 27). Calibration data are lacking.

Table 27. Method validation results for acetylcholinesterase essays on animal commodities.

Method reference	Commodity	LOQ report mg/kg eq	Spike, compound, mg/kg eq	Recovery mean, range	RSD_r	n	control mg/kg eq (n)	Calibration
Method B PA-705-009	cattle liver	0.1	P 0.1, 0.2, 0.5, 1.0 PO-SO2 0.1, 0.2, 0.5, 1.0	- 80-100 - 75-120	- -	1 1	<LOQ (3)	-
	cattle kidney	0.1	P 0.1, 0.2, 0.5, 1.0 PO-SO2 0.1, 0.2, 0.5, 1.0	- 84-110 - 94-127	- -	1 1	<LOQ (3)	
	cattle muscle	0.1	P 0.1, 0.2, 0.5, 1.0 PO-SO2 0.1, 0.2, 0.5, 1.0	- 70-100 - 98-115	- -	1 1	<LOQ (3)	
	cattle fat	0.1	P 0.1, 0.2, 0.5, 1.0 PO-SO2 0.1, 0.2, 0.5, 1.0	- 100-120 - 90-110	- -	1 1	<LOQ (3)	
	cattle milk	0.02	P 0.02 P 0.03 P 0.05 P 0.1 PO-SO2 0.02	100 80-120 109 100- 116 106 98- 120 100 100-	20% 7.4% 11% 0.0% 1.9%	3 3 3 3 3	<LOQ (10)	

Method reference	Commodity	LOQ report mg/kg eq	Spike, compound, mg/kg eq	Recovery mean, range	RSD$_r$	n	control mg/kg eq (n)	Calibration
			PO-SO2 0.03 PO-SO2 0.05 PO-SO2 0.1	100 91 90-93 93 90-95 103 100-105 102 99-105	3.1% 2.8% 3.0%	3 3 3		

LOQ report is LOQ listed in the study report, this LOQ is not necessarily the valid LOQ
n = number of samples used in recovery test at one concentration level
P = phorate, parent
PO-SO2 = phoratoxon, expressed as mg/kg eq

GC-FPD methods for plant commodities

From 1971 on, GC-FPD methods for determination of total phorate-related residues (oxidizable to phoratoxon sulfone) have been developed for a wide range of substrates. The methods are based on the extraction of the parent and its oxygenated metabolites phorate sulfoxide, phorate sulfone, phoratoxon, phoratoxon sulfoxide and phoratoxon sulfone with MeOH-DCM (10-90). The extracts are cleaned-up by hexane-ACN partitioning and treatment with activated charcoal. Phorate-related residues were oxidized to the common moiety metabolite, phoratoxon sulfone, using 3-chloroperoxybenzoic acid in DCM. The reaction mixture is cleaned-up by washing with sodium sulfite and bicarbonate solutions in water, precipitation of oily residues with aqueous ammonium chloride - phosphoric acid solution and water-DCM partitioning. The DCM is removed and the residue is redissolved in acetone, which is then analyzed by GC-FPD in phosphorus mode. GC conditions: packed column 3% OV-210 on Supelcoport 80/100 mesh deactivated with Carbowax 20M at 155-200 °C. Calibration by phorate standards which were run through the oxidation procedure (analyzed as phoratoxon sulfone). Oxidation efficiency was verified against a phoratoxon sulfone reference standard and should be at least 50% to start the analysis procedure.

The methods vary in the extraction solvent, in the clean-up procedures used before and after oxidation and in the GC-column conditions. The LOQ for most of the reported trials was 0.05 mg/kg eq. The methods have been validated on a wide range of substrates (see Table 28). In most cases only a limited number of recovery samples per concentration level (n<5), of compounds used for recovery checks (phorate and 5 oxidized metabolites), and of control samples analysed (n<2) were used. In other cases calibration data were lacking.

Table 28. Method validation results for GC-FPD methods on plants.

Method reference	Commodity	LOQ report mg/kg eq	Spike compound, mg/kg eq	Recovery mean range	RSD$_r$	n	control mg/kg eq (n)	Calibration
M-0455 PA-730-013	maize grain	0.05	P 0.05	80 -	-	1	< 0.3 LOQ (2)	3-5 x 4 points; range 5-30 ng; in acetone; linear by graph
			P 0.10	90 -	-	1		
			P 0.25	80 -	-	1		
			PO-SO2 0.05	100 -	-	1		
			PO-SO2 0.10	90 -	-	1		
			PO-SO2 0.25	104 -	-	1		
	green maize forage	0.05	P 0.05	88 -	-	1	< 0.3 LOQ (3)	
			P 0.10	80 -	-	1		
			P 0.25	90 -	-	1		
			PO-SO2 0.05	76 -	-	1		
			PO-SO2 0.10	65 -	-	1		
			PO-SO2 0.25	66 -	-	1		
	dry maize fodder	0.05	-	-	-	-	< 0.3 LOQ (2)	
M-1599	maize grain	0.01	P 0.01	81 76-86	6.0%	3	< 0.3 LOQ	-

Method reference	Commodity	LOQ report mg/kg eq	Spike compound, mg/kg eq	Recovery mean	range	RSD$_r$	n	control mg/kg eq (n)	Calibration
PA-244-032			P 0.05	81	78-86	5.6%	3	(4)	
			P 0.20	88	86-90	-	2		
M-1618 PA-244-033	maize grain	0.01	P 0.01	147	145-148	-	2	0.003-0.005 (2) LOQ = 0.02	-
			P 0.10	89	85-93	-	2		
	sweet corn cobs plus kernels	0.01	P 0.01	106	99-113	-	2	< 0.3 LOQ (2)	
			P 0.10	74	74-74	-	2		
	green maize forage	0.05	P 0.05	92	89-95	-	2	< 0.3 LOQ (2)	
			P 2.0	58	54-62	-	2		
	dry maize fodder	0.05	P 0.05	105	103-107	-	2	< 0.3 LOQ (2)	
			P 2.0	71	63-79	-	2		
modified M-1618 PA-244-008	maize grain	0.01	A 0.01	87	84-90	-	2	< 0.3 LOQ (2)	-
			A 0.05	90	84-95	-	2		
			A 0.20	79	75-82	-	2		
	dry maize fodder	0.05	A 0.05	106	100-111	-	2	< 0.3 LOQ (2)	
			A 0.10	103	102-103	-	2		
			A 1.0	87	84-90	-	2		
modified M-1618 PA-730-068	maize grain	0.01	P 0.010	74	55-92	-	2	< 0.3 LOQ (5)	-
			P 0.050	82	80-85	-	2		
			B 0.010	80	78-83	3.1%	3		
			B 0.025	86	74-102	17%	3		
			B 0.050	84	82-86	-	2		
M-1620 PA-244-030	potatoes	0.05	P 0.05	93	82-103	-	2	< 0.3 LOQ (2)	-
			P 0.1	105	81-129	-	2		
			P 0.2	102	-	-	1		
			P 0.5	111	97-125	-	2		
			P 1.0	100	-	-	1		
M-1653 PA-244-028	dry soya bean seeds	0.05	A 0.05	86	83-88	-	2	< 0.3 LOQ (2)	-
			A 0.1	97	95-99	-	2		
			A 1.0	89	87-91	-	2		
M-1683 PA-244-025	sugarbeet roots	0.05	P 0.10	87	82-92	-	2	< 0.3 LOQ (1)	-
			P 0.20	101	-	-	1		
			A 0.05	114	-	-	1		
			A 0.15	120	-	-	1		
			A 0.60	78	76-81	-	2		
			A 1.0	67	62-73	-	2		
	sugarbeet tops	0.05	P 0.20	88	-	-	1	< 0.3 LOQ (1)	
			A 0.05	83	79-87	4.6%	3		
			A 0.15	91	-	-	1		
			A 0.60	73	72-73	-	2		
			A 1.0	78	73-82	-	2		
M-1700 PA-244-021	cotton seeds	0.05	A 0.05	110	110-110	-	2	< 0.3 LOQ (2)	-
			A 0.10	122	114-131	-	2		
			A 1.0	96	95-97	-	2		
	dry cotton fodder	0.05	A 0.05	122	110-134	-	2	< 0.3 LOQ (2)	
			A 0.10	156	147-	-	2		
			A 1.0			-	2		

Method reference	Commodity	LOQ report mg/kg eq	Spike compound, mg/kg eq	Recovery mean range	RSD$_r$	n	control mg/kg eq (n)	Calibration
				165 99 88-110				
M-1705 PA-244-017	potato flakes	0.05	A 0.05 A 0.1 A 0.5 A 5.0	108 86-136 101 90-115 110 92-133 79 65-114	19% 11% 19% 23%	4 4 4 6	< 0.3 LOQ - 0.016 (3) LOQ = 0.06	-
	potato chips	0.05	A 0.05 A 0.1 A 0.5 A 5.0	105 91-114 95 94-97 84 81-87 73 61-88	9.3% - - 13%	4 2 2 6	< 0.3 LOQ (4)	
	potato granules	0.05	A 0.05 A 0.1 A 0.5 A 5.0	113 105- 132 97 79-114 87 84-89 81 66-98	12% - - 16%	4 2 2 4	< 0.3 LOQ - 0.027 (5) LOQ = 0.09	
M-1708 PA-244-018	sugarbeet roots	0.05	A 0.05 A 0.10 A 1.0	107 106- 107 89 87-92 91 90-92	- - -	2 2 2	< 0.3 LOQ (2)	-
	sugarbeet tops	0.05	A 0.05 A 0.10 A 1.0	99 98-100 88 71-105 92 86-98	- - -	2 2 2	< 0.3 LOQ (2)	
M-1718 PA-244-015	green beans (pods with seeds)	0.05	A 0.05 A 0.10 A 1.0	97 77-150 66 58-72 55 54-56	35% - -	4 2 2	< 0.3 LOQ (2)	-
	dry bean seeds	0.05	A 0.05 A 0.10 A 1.0	83 76-90 69 59-79 70 70-71	- - -	2 2 2	< 0.3 LOQ (2)	
M-1722 PA-244-016	sorghum grain	0.05	A 0.05 A 0.10 A 0.20 A 1.0	127 120- 133 90 39-124 92 87-97 107 75-125	- 39% - 26%	2 4 2 3	< 0.3 LOQ	-
	green sorghum forage	0.05	A 0.05 A 0.10 A 0.20 A 1.0	66 66-66 69 60-84 85 81-90 75 66-79	- 15% - 8.1%	2 4 2 4	< 0.3 LOQ (2)	
	dry sorghum fodder	0.05	A 0.05 A 0.10 A 1.0	78 72-84 76 50-102 92 92-92	- - -	2 2 2	< 0.3 LOQ (2)	

LOQ report is LOQ listed in the study report, this LOQ is not necessarily the valid LOQ
n = number of samples used in recovery test at one concentration level
- no data available
P = phorate,
PO-SO2 = phoratoxon sulfone, expressed as phorate
A = mixture of 1:1:1 phorate, phorate sulfoxide, phorate sulfone, expressed as phorate
B = mixture of 1:1:1:1:1:1 phorate, phorate sulfoxide, phorate sulfone, phoratoxon, phoratoxon sulfoxide, phoratoxon sulfone expressed as phorate

Method C was used in a modified version in 1981 supervised trials on sorghum. A full method description of the original method (version 14 May 1969) was available in Higham, 1969 (PA-730-004). Deviations from the general method were as follows: a) residues were extracted with chloroform; b) the only clean-up step was charcoal clean-up for forage/fodder and hexane-acetonitrile partitioning for grain; c) the oxidation reaction was carried out in chloroform; d) after oxidation the only clean-up step was washing with sodium sulfite and sodium bicarbonate followed by acetonitrile-hexane partitioning for forage/fodder; e) after oxidation the general clean-up is followed for grain, except that the final partitioning was between water-chloroform; f) GC conditions were modified: packed column 5% DC-200 on Gas-Chrom Q 60/80 mesh at 175 °C and CsBr thermionic detector; g) oxidation efficiency was not verified.

In the 1981 supervised trials on sorghum the GC-conditions were modified to 3% OV-210 column and GC-FPD detection as in the general method. A method validation report was not available and accuracy of residue concentrations is therefore unknown.

Method M-0165, version 3 March 1971, was used in 1981 supervised trials on maize. A full method description and validation report on cotton seed was available in Snyder and Gillespie, 1975 (PA-750-004). Deviations from the general method were as follows: a) residues were extracted with MeOH-chloroform (10-90); b) the charcoal clean-up step was omitted; c) the oxidation reaction was carried out in chloroform; d) the final clean-up was with water-chloroform partitioning; e) GC conditions were modified: packed column 5% DC-200 on Gas-Chrom Q 60/80 mesh at 190 °C; f) oxidation efficiency was not verified. A method validation report for maize commodities was not available and accuracy of residue concentrations is therefore unknown.

Method M-0455, version 7 Sept 1973, was used in 1971 supervised trials on maize. A full method description and validation report was available in Peterson, 1973 (PA-730-013). Deviations from the general method were as follows: a) residues were extracted with chloroform; b) hexane-ACN partitioning and activated charcoal clean-up were omitted; c) the oxidation reaction was carried out in chloroform; d) the final clean-up was with water-chloroform partitioning; e) GC conditions were modified: packed column 5% DC-200 on Gas-Chrom Q 60/80 mesh at 170-180 °C; f) oxidation efficiency was not verified. Recovery results for phoratoxon sulfone are not summarized because this compound was oxidized in situ and chemical purity is not known. Further it is not clear how the calibration for recovery tests with phoratoxon sulfone was carried out.

Method M-0684 was used in all coffee trials. No method description or validation report was available and accuracy of residue concentrations is therefore unknown.

Method M-1599, version 16 Dec 1985, was used in 1985 and 1990 supervised trials on maize and storage stability studies on maize. A full method description and validation report was available in Roman, 1985 (PA-244-032). There were no deviations from the general method. Recovery results for phorate sulfoxide and phorate sulfone were not summarized, because the results were obtained against oxidised phorate sulfoxide and oxidised phorate sulfone standards, respectively, not against oxidised phorate standards as used for the samples.

Method M-1618, version 25 Mar 1986, was used in 1985 supervised trials on maize and sweet corn and storage stability studies for maize. A full method description and validation report was available in Higham, 1986 (PA-244-033). There were no deviations from the general method. Recovery results for phorate sulfoxide and phorate sulfone were not summarized, because the results were obtained against oxidised phorate sulfoxide and oxidised phorate sulfone standards, respectively, not against oxidised phorate standards as used for the samples. Because of matrix interferences and high recovery values, the valid LOQ for maize grain was increased to 0.02 mg/kg eq. Likewise the LOQ was increased to 0.02 mg/kg eq for all maize grain samples from the 1985 trials analysed with method M-1618.

A modification of the method was used in the 1986 supervised trials on maize. Only minor modifications were introduced. A validation report was available in Higham, 1988 (PA-244-008).

A modification of the method was used in the 1994 supervised trials on maize. Various minor modifications were introduced and GC conditions were modified: capillary column DB-1701. A validation report for maize commodities was not available and accuracy of residue concentrations is therefore unknown.

Method M-1620, version 22 Apr 1986, was used in 1985, 1986, 1987, and 1988 supervised trials on potatoes and storage stability studies for potatoes. A full method description and validation report was available in Bohn, 1986 (PA-244-030). Deviations from the general method were as follows: a) residues were extracted with DCM; b) hexane-ACN partitioning and activated charcoal clean-up were omitted; c) precipitation and final water-dichoromethane partitioning were omitted. Recovery results for phorate sulfoxide and phorate sulfone were not summarized, because the results were obtained against oxidised phorate sulfoxide and oxidised phorate sulfone standards, respectively, not against oxidised phorate standards as used for the samples.

Method M-1634, was used on selected samples from 1985 supervised trials on green maize forage. This method determines phorate and 5 potential metabolites individually with GC-FPD. A method description and method validation report is not available and accuracy of residue concentrations is therefore unknown. It is not known if concentrations are expressed as mg/kg eq or as mg/kg for each metabolite individually.

Method M-1653, version 25 Nov 1986, was used in 1985 supervised trials on soya beans, 1990 supervised trials on dry beans and storage stability studies on dry beans. A full method description and validation report was available for soya beans in Higham, 1986 (PA-244-028). There were no deviations from the general method. A validation report for dry beans is not available and accuracy of residue concentrations is therefore unknown.

Method M-1672, was used in 1985 processing trials on maize (meal, oil) and a storage stability study on maize oil and maize meal. No method description and method validation report was available and accuracy of residue concentrations is therefore unknown.

Method M-1683, version 19 Nov 1986, was used in some 1985 supervised trials on sugar beets and storage stability studies for sugar beets. A full method description and validation report was available in Peterson, 1987 (PA-244-025). The deviations from the general method were as follows: a) residues in sugarbeet roots were extracted with MeOH-DCM (10-90), while sugarbeet tops were extracted with DCM; b) hexane-ACN partitioning and charcoal clean-up were omitted.

Method M-1700, version 14 Jan 1987, was used in 1985 supervised trials on cotton seed. A full method description and validation report was available in Higham, 1987 (PA-244-021). There were no deviations from the general method. Because of high method recoveries, results below 1 mg/kg eq in cotton seed and dry fodder must be considered as inaccurate and consequently results below 1 mg/kg eq for all 1985 trials must not be used for MRL derivation.

Method M-1705, version 26 Jan 1987, was used in 1986, 1987, 1990, and 1991 processing trials on potatoes. A full method description and validation report was available in Khunachak, 1987 (PA-244-017). Deviations from the general method were as follows: a) residues were extracted with aqueous MeOH, followed by partitioning into DCM; b) the hexane-ACN partitioning was omitted; c) the washing step after oxidation was omitted; d) after final water-DCM partitioning an additional clean-up with C18 SPE was added; e) calibration was carried out with an oxidized combination standard containing phorate, phorate sulfoxide and phorate sulfone in equal amounts (w/w/w). Because of matrix interferences, the valid LOQ was increased to 0.06 mg/kg eq for potato flakes and 0.09 mg/kg eq for potato granules. Likewise the LOQ was increased to for flake and granule samples from the 1985, 1987, 1990, 1991 processing trials on potatoes. A method validation report on raw potatoes (+/- peel), raw peels, cooked potatoes (+/- peels), cooked peels, baked potatoes (+/- peel), baked peels, dry peels, french fries, wash or cooking water is not available and accuracy of residue concentrations is therefore unknown.

A modification of the method was used in 1990 supervised trials on potatoes in Canada. In most cases a 10% OV-101 column was used, however in some cases the default 3% OV-210 column was used. A method validation report for the modified method is not available and accuracy of residue concentrations is therefore unknown.

Method M-1706, was used in 1985 processing trials on maize (grits, flour, hulls, presscake). No method description and method validation report was available and accuracy of residue concentrations is therefore unknown.

Method M-1708, version 10 Febr 1987, was used in some 1985 supervised trials on sugarbeets. A full method description and validation report was available in Higham, 1987 (PA-244-018). The deviations from the general method were as follows: the hexane-ACN partitioning was omitted.

Method M-1718, version 17 Mar 1987, was used in 1985 and 1993 supervised trials on green beans and in 1985 supervised trials on dry beans. A full method description and validation report was available in Higham, 1987 (PA-244-015). There were no deviations from the general method. Low recoveries were found at 0.05-0.10 mg/kg eq (<70%) and high RSD_r at 0.01 mg/kg eq (>20%).

Method M-1722, version 26 Mar 1987, was used in 1985, 1990, and 1993 supervised trials on sorghum. A full method description and validation report is available in Higham, 1987 (PA-244-016). There were no deviations from the general method. For sorghum grain, high recoveries were found at 0.01 mg/kg eq (>120%) and high RSD_r (>20%) at concentrations between 0.1-1.0 mg/kg eq. For green forage and dry fodder low recoveries (< 70%) at concentrations below 0.2 mg/kg eq were found.

Method M-1724, was used in 1985 processing trials on maize (germ). No method description and method validation report was available and accuracy of residue concentrations is therefore unknown.

Method M-1734, was used in 1985 processing trials on maize (soapstock). No method description and method validation report was available and accuracy of residue concentrations is therefore unknown.

GC-methods in animal commodities

From 1971 on, GC methods for determination of total phorate-related residues (oxidizable to phoratoxon sulfone) have been developed for animal commodities. The methods are based on the extraction of the parent and its oxygenated metabolites phorate sulfoxide, phorate sulfone, phoratoxon, phoratoxon sulfoxide and phoratoxon sulfone with ACN. The extracts are cleaned-up by hexane-ACN partitioning to remove fat, followed by GPC. Phorate-related residues were oxidized to the common moiety metabolite, phoratoxon sulfone, using 3-chloroperoxybenzoic acid in DCM. The reaction mixture is cleaned-up by washing with sodium sulfite and sodium bicarbonate solution, by precipitation of fatty residues with aqueous ammonium chloride - phosphoric acid solution and water-chloroform partitioning. Egg extracts are further cleaned-up by florisil adsorption chromatography. The final extract is evaporated to dryness and redissolved in acetone, which is then analyzed by GC with a phosphorus specific detector. Calibration by phorate or mixed phorate-related compounds which were run through the oxidation procedure (analyzed as phoratoxon sulfone). Oxidation efficiency was verified against a phoratoxon sulfone reference standard and should be at least 50% to start the analysis procedure. The methods have been validated for animal commodities (see Table 29).

In most cases a limited number of recovery samples per concentration level (n < 5), of compounds used for recovery checks (phorate and 5 oxidized metabolites), and of control samples analysed (n < 2) were tested. In other cases calibration data were lacking.

Table 29. Method validation results for GC methods in animal commodities.

Method reference	Commodity	LOQ report mg/kg eq	Spike compound, mg/kg eq	Recovery mean range	RSD_r	n	control mg/kg eq (n)	Calibration
Method D PA-705-001	chicken liver	0.05	P 0.05	106 -	-	1	< 0.3 LOQ (3)	-
			P 0.10	108 -	-	1		
			P 0.20	92 90-94	-	2		
	chicken kidney	0.05	P 0.05	125 -	-	1	< 0.3 LOQ (3)	
			P 0.10	81 -	-	1		
			P 0.20	113 -	-	1		
	chicken muscle	0.05	P 0.05	114 -	-	1	< 0.3 LOQ (3)	
			P 0.10	85 76-101	16%	3		

Method reference	Commodity	LOQ report mg/kg eq	Spike compound, mg/kg eq	Recovery mean	range	RSD$_r$	n	control mg/kg eq (n)	Calibration
			P 0.20	90	-	-	1		
	chicken fat	0.05	P 0.05	68	-	-	1	< 0.3 LOQ - 0.017 (3) LOQ=0.06	
			P 0.10	80	69-90	-	2		
			P 0.20	63	-	-	1		
	chicken eggs	0.05	P 0.05	85	-	-	1	< 0.3 LOQ (3)	
			P 0.10	91	-	-	1		
			P 0.20	114	-	-	1		
M-2461 PA-245-003 ILV	cattle liver	0.02	B 0.02	89	81-97	-	2	< 0.3 LOQ (2)	-
			B 0.1	88	71-105	-	2		
	cattle kidney	0.02	B 0.02	102	93-110	-	2	< 0.3 LOQ (2)	
			B 0.10	114	109-120	-	2		
	cattle muscle	0.02	B 0.02	118	116-119	-	2	< 0.3 LOQ (2)	
			B 0.10	121	113-129	-	2		
	cattle fat	0.02	B 0.02	110	107-112	-	2	< 0.3 LOQ (2)	
			B 0.10	114	109-119	-	2		
M-2469 PA-245-003 ILV	cattle milk	0.005	B 0.005	96	95-96	-	2	< 0.3 LOQ (2)	-
			B 0.05	94	91-98	-	2		

LOQ report is LOQ listed in the study report, this LOQ is not necessarily the valid LOQ
n = number of samples used in recovery test at one concentration level
- no data available,
ILV = independent laboratory validation
P = phorate
B = mixture of 1:1:1:1:1:1 phorate, phorate sulfoxide, phorate sulfone, phoratoxon, phoratoxon sulfoxide, phoratoxon sulfone expressed as phorate

Method D was used in 1969 feeding studies on poultry tissues. A full method description and validation report was available in Higham, 1969 (PA-705-001). Deviations from the general method were as follows: a) residues were extracted with DCM for liver, kidney and eggs or ACN for fat; b) GPC was omitted; c) oxidation was carried out in chloroform; d) GC-conditions were: packed column 5% DC-200 on Gas-Chrom Q, 60/80 mesh, at 170 °C; f) a caesium bromide thermionic detector was used; g) calibration was carried out with oxidized parent compound; h) oxidation efficiency was not verified. Recovery results for phoratoxon sulfone are not summarized because this compound was oxidized in situ and chemical purity is not known. Further it is not clear how the calibration for recovery tests with phoratoxon sulfone was carried out. Because of matrix interferences the LOQ for fat was increased to 0.017/0.3=0.06 mg/kg eq.

Method M-2461, version 2 Nov 1995, was used in 1995 feeding studies on dairy cattle. A full method description and validation report was available in Khunachak and Witkonton, 1995 (PA-245-003). Deviations from the general method were as follows: a) precipitation clean-up and water-chloroform partitioning after oxidation were omitted; b) GC-conditions were: capillary column DB-1 at 140 °C; c) a flame photometric detector in phosphorus mode was used; d) calibration was carried out with a mixed standard containing equal amounts of phorate, phorate sulfoxide, phorate sulfone, phoratoxon, phoratoxon sulfoxide and phoratoxonsulfone (w/w/w/w/w/w). The method was independently validated by a second laboratory. Results for the first laboratory were not submitted.

Method M-2469, version 2 Nov 1995, was used in 1995 feeding studies on dairy cattle and storage stability studies on milk. A full method description and validation report was available in Khunachak and Witkonton, 1995 (PA-245-003). Deviations from the general method were as follows: a) milk was extracted with acetone and DCM; b) gel permeation clean-up was omitted; c) washing after oxidation was only carried out with sodium sulfite; d) precipitation clean-up and water-chloroform partitioning were omitted; e) GC-conditions were: capillary column DB-1 at 140 °C; f) a flame photometric detector in phosphorus mode was used; g) calibration was carried out with a mixed standard containing equal amounts of phorate, phorate sulfoxide, phorate sulfone, phoratoxon, phoratoxon sulfoxide and phoratoxonsulfone (w/w/w/w/w/w). The method was independently validated by a second laboratory. Results for the first laboratory were not submitted.

Stability of pesticide residues in stored analytical samples

The Meeting received data on the stability of residues in dry beans, potatoes, sugarbeets, and maize stored frozen. In addition, the Meeting received data on the stability of residues in milk stored frozen.

Green beans (with or without pods)

No storage data are available on green beans (seeds, seeds with pods). Storage data for sugarbeet tops or green maize forage/fodder may be extrapolated to green beans (seeds, seeds with pods).

Dry bean seeds

Untreated samples of dry bean seeds were fortified with 0.3 mg/kg eq of a mixed standard consisting of 0.1 mg/kg each of phorate, phorate sulfoxide, and phorate sulfone or with 0.3 mg/kg eq of another mixed standard consisting of 0.1 mg/kg each of phoratoxon, phoratoxon sulfoxide, and phoratoxon sulfone. The samples were stored frozen at -10°C or lower for periods of up to two years (Higham, 1994: PA-326-002 and Higham, 1995: PA-326-016). Three replicate samples were analysed using GC-FPD as described in method M-1653. The reported LOQ was 0.05 mg/kg eq. A validation report for dry beans is not available and accuracy of residue concentrations is therefore unknown.

Results are shown in Table 30. Samples were not corrected for concurrent method recovery (80%–116%), but were corrected for matrix interferences (up to 0.023 mg/kg eq). Results show that total phorate-related residues (oxidizable to phoratoxon sulfone) are stable in dry bean samples up to two years when stored frozen at approximately -10°C to -20°C.

Table 30. Freezer storage stability of total phorate-related residues (oxidizable to phoratoxon sulfone) on dry bean seeds (n=3) fortified with 0.3 mg/kg eq and stored at approximately –10°C or lower for a periods up to two years.

Compounds	Interval (months)	Total residues % remaining			Concurrent recovery
		mean	range	RSD_r	
Mixed standard of phorate, phorate sulfoxide, and phorate sulfone (each 0.1 mg/kg eq)	0	101%	91%-114%	12%	92%
	1	95%	89%-101%	6.3%	111%
	3	85%	81%-87%	3.6%	102%
	6	91%	82%-99%	9.4%	105%
	12	94%	85%-102%	9.1%	104%
	18	99%	96%-103%	3.8%	109%
	24	85%	80%-90%	6.1%	80%
Mixed standard of phoratoxon, phoratoxon sulfoxide, and phoratoxon sulfone (each 0.1 mg/kg eq)	0	95%	88%-108%	12%	115%
	1	no data reported			
	3	84%	71%-94%	14%	116%
	6	75%	71%-81%	7.1%	88% (68%, 108%)
	12	68%	64%-74%	7.5%	96% (95%, 97%)
	18	70%	64%-75%	8.1%	101%
	24	85%	80%-89%	5.5%	93%

Potato tubers

Untreated samples of potato tubers were ground and fortified with 0.15 mg/kg eq of a mixed standard consisting of 0.5 mg/kg each of phorate, phorate sulfoxide, and phorate sulfone (Bohn, 1987: PA-325-014 and PA-326-005). Samples were stored at -23 °C or lower for a period of 706 d. Samples were analysed for total phorate-related residues (oxidizable to phoratoxon sulfone) using GC-FPD, following method M-1620. The reported LOQ was 0.05 mg/kg eq.

The results are summarised in Table 31. Samples were not corrected for matrix interferences (< 0.3 LOQ). Concurrent method recoveries were not verified and therefore performance of the method at the time of sample analysis is unknown.

Table 31. Freezer storage stability of total phorate-related residues (oxidizable to phoratoxon sulfone) on potato tubers fortified with 0.15 mg/kg eq and stored at approximately -23 °C or lower for a period up to 706 days.

Compound	Interval (d)	Total residues % remaining
Mixed standard of phorate, phorate sulfoxide, and phorate sulfone (0.5 mg/kg eq each)	0	98%
	93	85%
	199	80%
	490	76%
	668	43%
	706	96%

Some potato samples from a 1987 USA trial were not analysed until 2.5 years after collection (Dixon and Gorrell, 1990, PA-724-012 and PA-724-016). To show that residues were stable during the freezer storage period at -10 °C or lower, two samples were analyzed at 13–18 months after collection and at 2.5 years after collection. The samples were analysed by GC-FPD, following method M-1620. The reported LOQ was 0.05 mg/kg eq.

Results are shown in Table 32. Samples were not corrected for concurrent method recoveries (68 %–117%), or for matrix interferences (< 0.3 LOQ). Results from day 0 samples were not available and therefore the percent remaining cannot be calculated.

Table 32. Freezer storage stability of total phorate-related residues (oxidizable to phoratoxon sulfone) on potato tubers with incurred residues and stored at approximately –10 °C from 13 months to 2.5 years.

Report, sample no	Total, mg/kg eq day 0	Total, mg/kg eq 13 months	Total, mg/kg eq 18 months	Total, mg/kg eq 2.5 years
PA-724-012, 6755.3	no data	0.14	-	0.083, 0.13; mean 0.11
PA-724-016, 6783.1	no data	-	0.18	0.15, 0.16; mean 0.16

Results show that total phorate-related residues (oxidizable to phoratoxon sulfone) in potato tubers are stable up to 2.5 years when stored at -10°C or lower.

Processed potato commodities

No data submitted.

Sugarbeet roots and tops

Untreated samples of ground sugarbeet roots and tops were fortified with 0.15 mg/kg eq of a mixed standard containing 0.05 mg/kg each of phorate, phorate sulfoxide, and phorate sulfone. The samples were stored at –23 °C or lower for a period of 695 d (Peterson, 1987: PA-326-011 and PA-326-009). Total phorate-related residues (oxidizable to phoratoxon sulfone) were analysed by GC-FPD according to method M-1683. The reported LOQ was 0.05 mg/kg eq.

Results are shown in Table 33. Samples were not corrected for matrix interferences (< 0.3 LOQ). Concurrent method recoveries were not verified and therefore performance of the method at the time of sample analysis is unknown. The results show that total phorate-related residues (oxidizable to phoratoxon sulfone) are stable up to 695 d when stored at –23 °C or lower.

Table 33. Freezer storage stability of total phorate-related residues (oxidizable to phoratoxon sulfone) on sugarbeet roots and tops fortified with 0.15 mg/kg eq and stored at approximately –23 °C or lower for a period up to 695 days.

Commodity	Compounds	Interval (d)	Total residues % remaining
Sugarbeet roots	Mixed standard of phorate, phorate sulfoxide, and phorate sulfone (0.05 mg/kg eq each)	1	90 (108, 72)
		90	88
		378	113
		695	78
Sugarbeet tops	Mixed standard of phorate, phorate sulfoxide, and phorate sulfone (0.05 mg/kg eq each)	1	73
		90	66
		378	85
		695	103

Maize commodities (grain, green forage, dry fodder)

The freezer storage stability of total phorate-related residues (oxidizable to phoratoxon sulfone) was studied in maize commodities (Roman, 1987: PA-326-015 and PA-326-007 and Roman 1988: PA-326-003). Control samples of maize grain and maize straw (dry fodder) were fortified with a mixed standard consisting of 1:1:1 ratio of phorate, phorate sulfoxide, and phorate sulfone. Total fortification levels were 0.06 mg/kg eq for maize grain and 0.3 mg/kg eq for maize straw. Green maize plants (green forage) were fortified at a level of 0.6 mg/kg eq with a mixture composed of equal parts of phorate, phorate sulfoxide, and phorate sulfone, phoratoxon, phoratoxon sulfoxide and phorate oxon sulfone. Samples were stored at -23 °C or lower for a period of 24 months. Samples were analysed by GC-FPD, using method M-1599 for maize grain and M-1618 for green maize plants and straw. The reported LOQ was 0.01 mg/kg eq for grain and 0.05 mg/kg eq for green maize plants and straw.

The results are summarised in Table 34. Samples were not corrected for matrix interferences (< 0.3 LOQ) or for concurrent method recovery (85%-101%). Concurrent method recoveries were not verified for a number of samples and therefore performance of the method at the time of sample analysis is unknown. The results indicate that total phorate-related residues (oxidizable to phoratoxon sulfone) in maize grain, green maize plants and maize straw are stable for at least 24 months when samples are kept frozen at –23°C or lower.

Table 34. Freezer storage stability of total phorate-related residues (oxidizable to phoratoxon sulfone) on samples of maize grain, green maize plants and straw fortified and stored at–23°C or lower for a period up to 24 months.

Commodity	Compound	Interval (d)	Total residues % remaining	Concurrent recovery (%)
Maize grain	Mixed standard of phorate, phorate sulfoxide, and phorate sulfone (each 0.02 mg/kg eq)	0	92	-
		3	118	-
		6	96	-
		12	97	-
		19	96	90%
		24	87	100%
Green maize plants (green forage, green fodder)	Mixed standard of phorate, phorate sulfoxide, phorate sulfone, phoratoxon, phoratoxon sulfoxide and phoratoxon sulfone (each 0.1 mg/kg eq)	0	100	-
		3	115	-
		6	100	-
		12	97	-
		19	98	97%
		24	100	101%
Maize straw (dry fodder)	Mixed standard of phorate, phorate sulfoxide, and phorate sulfone (each 0.1 mg/kg eq)	0	90	-
		3	83	-
		11	87	92%
		17	83	85%
		24	91 (89, 92)	93%

Processed maize commodities (meal, refined oil)

The stability of total phorate-related residues (oxidizable to phoratoxon sulfone) was studied in maize meal and refined oil (Potts, 1987: PA-326-010, PA-326-006 and PA-326-008). Processed maize meal and refined oil samples containing actual field incurred residues taken from the processing laboratory were used for the study. All samples were kept at -23°C or lower for 12 months. Samples were analysed by GC-FPD, according to method M-1672. The reported LOQ was 0.05 mg/kg eq for all commodities. No method description and method validation report was available and accuracy of residue concentrations is therefore unknown.

The results are summarised in Table 35. Samples were not corrected for matrix interferences (< 0.3 LOQ for oil and meal). Concurrent method recoveries were not verified and therefore performance of the method at the time of sample analysis is unknown. Storage stability studies were undertaken after the first analysis of the processed commodities. Information on stability of the first 311-345 d of storage, before first analysis, is lacking. However, since the study was undertaken with field incurred residues, and total phorate-related residues are measured, the results are acceptable for evaluation.

Table 35. Freezer storage stability of incurred total phorate-related residues (oxidizable to phoratoxon sulfone) in samples of maize meal and refined maize oil stored at approximately –23°C or lower.

Location, year, (variety)	Form, kg ai/ha	DAT	Commodity	Interval (d)	Total mg/kg eq	% remaining	Reference
Monticello, IL, USA; 1985 (T-1100)	200 G 1x 7.29 1x 7.29 1x 5.60	30	maize meal	+0 [a] +74 +178 +362	0.17 0.26 0.16 0.23	100% 153% 94% 135%	Potts, 1986 [PA-730-042] Potts, 1987 [PA-326-006] [PA-326-008]
Monticello, IL, USA; 1985 (T-1100)	200 G 1x 7.29 1x 7.29 1x 5.60	30	maize refined oil	+0 [a] +103 +221 +397	0.36 0.34 0.22 [b] 0.38	100% 94% 61% 106%	idem

[a] Day 0 is the first analysis result for maize meal and refined oil. But after processing these commodities have been stored at -23 °C or lower and the time period between processing and first analysis is unknown but is maximally 311-345 d. Any decline in residue during this first period remains unnoticed.

[b] Average of duplicate analysis.

Cotton

No storage data are available on cotton (seeds, dry fodder). Storage data for dry maize fodder may be extrapolated to cotton dry fodder.

Coffee beans

No storage data submitted.

Animal commodities

Storage data are only submitted on cow milk. No storage data are submitted on tissues (poultry, ruminants) and eggs. Ruminant tissues, from a cow feeding study, were stored for less than one month and therefore storage data on these tissues were not needed. Storage data on poultry tissues is however lacking.

Samples of freshly obtained control cow’s milk were fortified at a level of 0.025 mg/L of a mixture of standards containing phorate, phorate sulfoxide, phorate sulfone, phoratoxon, phoratoxon sulfoxide and phoratoxon sulfone, each at 0.0042 mg/L eq (Khunachak, 1995: PA-326-017 and

Khunachak, 1998: PA-705-007). Samples were stored in glass containers, either in the refrigerator (temperature not stated) for 4 days or in the freezer at -20 °C or lower for 18 months. Samples were analysed for total phorate-related residues (oxidizable to phoratoxon sulfone) using GC-FPD, as described in method M-2469. The reported LOQ was 0.005 mg/L eq.

The results are summarised in Table 36. Samples were not corrected for matrix interferences (< 0.3 LOQ) or for concurrent method recovery (88%-106%). The results show that total phorate-related residues (oxidizable to phoratoxon sulfone) are stable in cow's milk for at least 4 days when stored in the refrigerator and at least 18 months when stored in the freezer at -20 °C or lower.

Table 36. Refrigerator and freezer storage stability data of total phorate-related residues (oxidizable to phoratoxon sulfone) in samples of cow's milk fortified at 0.025 mg/L eq and stored refrigerated for 4 d or frozen at -20 °C or lower for a period up to 18 months.

Sample	Compounds	Interval (days or months)	Total residues % remaining mean	range	Concurrent recovery (%)
Refrigerated samples	Mixed standard of phorate, phorate sulfoxide, phorate sulfone, phoratoxon, phoratoxon sulfoxide and phoratoxon sulfone (each 0.0042 mg/L eq)	0 d	98	94, 102	91
		2 d	84	78, 90	88
		4 d	85	80, 90	94
Frozen samples	Mixed standard of phorate, phorate sulfoxide, phorate sulfone, phoratoxon, phoratoxon sulfoxide and phoratoxon sulfone (each 0.0042 mg/L eq)	0 month	90	88, 91	97
		1 month	88	78, 97	93
		2 months	100	100, 102	98
		3 months	93	92, 94	106
		6 months	101	99, 103	104
		12 months	88	88, 88	93
		18 months	104	102, 106	106

USE PATTERN

Phorate is a systemic and contact organophosphorus insecticide/nematicide. It is formulated as a granule for application to crops and soil. It is usually applied once at planting, but in some cases a second application may be necessary at cultivation. Target pests controlled by phorate include aphids, beetles, bugs, coffee cicadas, flies, white grubs, rice hispa, jassids, leafhoppers, leafminers, maggots, mites, plant hoppers, psyllids, stemborers, thrips, weevils, and worms.

Phorate is authorised for use as insecticide/nematicide in Australia, Brazil, Canada, Columbia, India, South Africa, and the USA on citrus, apple, banana, onion, brassica (broccoli, Brussels sprouts, cabbage, cauliflower), fruiting vegetable (chili pepper, egg plant, tomato, sweet corn), lettuce, pulses (beans, black gram, mung beans, pigeon peas, soya beans), root and tuber vegetables (carrot, potato, swede, sugarbeet), cereals (barley, maize, millet, rice, sorghum, wheat), sugarcane, oilseeds (cotton, mustard seeds, peanut, sesame seeds), and coffee beans. Further phorate is used for ornamentals.

Because residue trials were only available on legume vegetables (green beans, green snap beans), pulses (dry beans, dry soya beans), root and tuber vegetables (potato, sugarbeet), cereals (sweet corn, maize, sorghum), oilseeds (cotton), and coffee, only the uses on these crops and related crops are summarized in Table 37. For all uses original labels were available. For Australia, label information was confirmed by the national government. Phorate is not authorised for use in The Netherlands.

Table 37. Registered uses of soil treatments with granular formulations of phorate.

Crop	Country	Formulation g ai/kg	Application				PHI, d
			Method	Rate, kg ai/ha	Spray conc	Number	
Barley	India	100 G	Soil incorporated	1.0	na	1	42
Beans	Brazil	150 G	Soil incorporated at planting next to seeds	1.0 – 1.5	na	1	-
Beans	Canada	150 G	Soil incorporated at planting next to seeds	1.1-2.2	na	1	PHI na WP 60
Beans	USA	200 G	Soil incorporated at planting as a band or drilled next to seeds	1.1 – 2.3 [n]	na	1	60 WP = l
Black gram (dry)	India	100 G	Soil incorporated	1.0	na	1	42
Carrots	Australia[a]	100 G; 200 G	soil incorporated as a band at sowing or in 5 cm band on each side of established crop	1.0	na	1	PHI 70 WP 70
Coffee beans[b]	Brazil	150 G	Soil incorporated around the plant 5-10 cm depth	5.0 – 6.2	na	1	90
Coffee beans[b]	India	100 G	Soil incorporated	2.5	na	1	42
Cotton	Australia[a]	100 G; 200 G	soil incorporated at planting: in furrow or as side dressing	0.6 – 1.7	na	1	PHI 70; WP 70
Cotton	Brazil	150 G	Soil incorporated at planting in furrow or 10 d after emergency in covering beside the plant	2.0	na	1	-
Cotton	India	100 G	Soil incorporated	1.0	na	1	42
Cotton	South Africa	100 G	Soil incorporated	1.0[o]	na	1	84
Cotton	USA	200 G	Soil incorporated at planting in furrow or as a side dressing	0.61 - 2.4 [n]	na	1	60 WP = l
Maize [c]	Brazil	150 G	Soil incorporated at planting in furrow	2.6	na	1	-
Maize [c]	Canada	150 G	Soil incorporated at planting as band	1.25-1.50 [q]	na	1	-
Maize	India	100 G	Soil incorporated	1.0 - 3.0	na	1	42
Maize	South Africa	100 G	Soil incorporated	0.5[o]	na	1	60
Maize[c]	USA	200 G	Soil incorporated at planting as a band or at cultivation at the base of the plants	1.1 - 1.5 [n]	na	1	PHI 30 WP 30
Millet, bulrush [d]	India	100 G	Soil incorporated	2.5 - 3.0	na	1	42
Mung bean [e] (dry)	India	100 G	Soil incorporated	1.0 - 1.5	na	1	42
Mustard seeds [f]	India	100 G	Soil incorporated	1.0 - 1.5	na	1	42
Peanut [g]	India	100 G	Soil incorporated	1.5 - 2.5	na	1	42
Peanut	USA	200 G	Soil incorporated at planting in furrow	1.3 [n]	na	1	90 WP = l
Pigeon pea (dry)	India	100 G	Soil incorporated	1.0 - 1.5	na	1	42
Potato	Australia[a]	100 G; 200 G	soil incorporated at planting: in furrow or as a band on each side of the row	1.6 – 2.9	na	1	PHI 91; WP 70
Potato	Brazil	150 G	Soil incorporated at planting in furrow or half in furrow and half in covering	3.0	na	1	-
Potato	Canada	150 G	Soil incorporated at planting in furrow or as a band on each side of the row	2.3 -4.3 [q]	na	1	90
Potato	Colombia	50 G	soil incorporated 1st at planting in furrow; 2nd at complete germination	1.5 - 2.0	na	1-3	-

Crop	Country	Formulation g ai/kg	Application				PHI, d
			Method	Rate, kg ai/ha	Spray conc	Number	
			3rd before blanching				
Potato	India	100 G	Soil incorporated	1.0	na	1	42
Potato	South Africa	100 G	Soil incorporated	2 - 3[o]	na	1	90
Potato	USA	200 G	Soil incorporated at planting in furrow; at planting or 4-6 weeks after planting as a band on each side of the row	1.9 - 4.0 [n]	na	1	90
Rice [h]	India	100 G	Soil incorporated	0.75 – 1.0	na	1	PHI 42 WP 10
Sesame seed [i]	India	100 G	Soil incorporated	1.0	na	1	42
Sorghum	India	100 G	Soil incorporated	1.9 – 2.5	na	1	42
Sorghum	USA	200 G	Soil incorporated at planting as a band over the row or drilled next to the seeds; at cultivation at the base of established plants	1.1 - 1.5 [n]	na	1	30 WP = m
Soya bean [j] (dry)	India	100 G	Soil incorporated	1.5	na	1	42
Soya bean [j]	USA	200 G	Soil incorporated at planting as a band over the row or drilled next to the seeds	1.7 [n]	na	1	WP = l
Swede [k]	Canada	150 G	Soil incorporated at planting on top of the ridges or as a band before seeding	4.2-10.2 [q]	na	1	-
Sugarbeets	USA	200 G	Soil incorporated at planting as a band over the row or drilled next to the seeds; post-emergence at the base of established plants	1.1- 1.7 [n]	na	1	30
Sweet corn	USA	200 G	Soil incorporated at planting as a band; at cultivation at the base of established plants	1.1 - 1.5 [n]	na	1	PHI 30 WP 30
Wheat	India	100 G	Soil incorporated	1.9	na	1	42
Wheat	South Africa	100 G	Soil incorporated	1.0[p]	na	1	90

PHI = pre-harvest interval in d, WP = withholding period for livestock in DAT

a. GAP information confirmed by national government.

b. This crop was listed as coffee on the label, but the Codex name is used in the table (SB 0716).

c. This crop was listed as corn (Brazil, Canada) or field corn (USA), but the Codex name is used in the table. This crop is listed in Codex under two numbers: GC 4613 corn and GC 0645 maize.

d. This crop was listed as bajra on the label, but the Codex name is used in the table. Bajra is a millet type cereal grown in India (*Pennisetum typhoides*). This crop is listed in Codex under several numbers: GC 4607 bulrush millet; GC 4647 millet, bulrush; GC 4661 pearl millet.

e. This crop was listed as green gram on the label, but the Codex name is used in the table. This crop is listed in Codex under two numbers: VD 4493 green gram (dry) and VD 0536 mung bean (dry).

f. This crop was listed as mustard on the label, but the Codex name is used in the table (SO 0090).

g. This crop was listed as ground nut on the label, but the Codex name is used in the table. This crop is listed in Codex under several numbers: SO 4713 groundnut, SO 0697 peanut and SO 0703 peanut, whole.

h. This crop is listed as paddy on the label, but the Codex name is used in the table (GC 0649).

i. This crop is listed as sesamum on the label, but the Codex name is used in the table (SO 0700).

j. This crop was listed as soybean on the label, but the Codex name is used in the table. This crop is listed in Codex under two numbers: VD 0541 soya bean (dry) and VD 4521 soybean (dry).

k. This crop was listed as rutabaga on the label, but the Codex name is used in the table. This crop is listed in Codex under two numbers: VR 4563 rutabaga and VR 0497 swede.

l. Do not graze or feed treated hay or forage to livestock (beans, cotton, peanuts, soybean).

m. Do not feed foliage before grain harvest (sorghum)

n. Calculated by reviewer from oz product per 1000 ft row length and a minimum row spacing of 35 inch (beans, cotton, maize, sorghum, soya bean, sweet corn) or 32 inch (potato) or 24 inch (peanuts) or 20 inch (sugar beets).

o No row spacing is indicated in the label. A minimum row spacing of 100 cm is assumed by the manufacturer to calculate the dose rate.

The dose rate is calculated from g product per 100 m plant row and a minimum row spacing of 100 cm

p Calculated by reviewer from g product per 100 m plant row and minimum row spacing 35 cm.

q Calculated by reviewer from g product per 100 m plant row, and row spacing 75-90 cm for maize, potatoes, and swedes.

RESIDUES RESULTING FROM SUPERVISED TRIALS ON CROPS

The Meeting received information on supervised trials of soil treatments with phorate for the following crops:

Group	Table	Commodity
Fruiting vegetables other than cucurbits	38	Sweet corn
Legume vegetables	39-40	Green beans
Pulses	41	Dry beans
	42	Dry soya beans
Root and tuber vegetables	43	Potato
	44	Sugarbeets
Cereals	45	Maize (field corn)
	46	Sorghum
Oilseeds	47	Cotton
Seeds for beverages	48	Coffee beans
Straw, fodder and forage of cereal grains and grasses	49	Sweet corn forage
	50	Maize forage
	51	Maize fodder
	52	Maize fodder, metabolites
	53	Sorghum forage
	54	Sorghum fodder
Miscellaneous fodder and forage groups	55	Cotton fodder, dry
	56	Sugar beet tops

The results of supervised trials are shown in Tables 38 to 56. Where multiple samples were taken from a single plot individual and average values are reported. Where multiple analyses were conducted on a single sample, the average value is reported. Where results from separate plots with distinguishing characteristics such as different formulations, varieties or treatment schedules were reported, results are listed for each plot. Underlined values were used for the estimation of MRLs and STMRs. Results have not been corrected for concurrent method recoveries.

Fruiting vegetables other than cucurbits

Sweet corn

Nine trials were conducted on sweet corn in the USA in 1985. Phorate granular (GR) formulation was applied either as a single banded application at planting or as a double application: one in a band at planting followed by a band at cultivation. Rates per application ranged from 1.46 to 7.29 kg ai/ha.

Plot size was 56-138 m^2 at a row width of 76-91 cm. Random samples of sweet corn (kernels plus cob with husk removed) and sweet corn plants (immature with grains) were collected. Sampling details were not stated. Sample size was not stated. Samples were stored frozen at -10°C or lower. Total storage time was not stated, but was maximally 155 to 295 d which is covered by the 24 month storage stability study on maize commodities. Total phorate-related residues (oxidizable to phoratoxon sulfone) were determined by GC-FPD following method M-1618. The reported LOQ was 0.01 mg/kg eq for sweet corn and 0.05 mg/kg eq for green sweet corn forage. All samples were analysed on an as received basis.

Phorate residues in sweet corn kernels plus cob are summarised in Table 38 and Table 49 (green plants from sweet corn). Samples were not corrected for concurrent method recoveries (84%–91% for sweet corn, 64%–92% for green sweet corn plants) nor for matrix interferences (< 0.3 LOQ for grain and plants). Due to matrix interferences in control samples, the valid LOQ for green plants was increased to 0.016/0.3=0.06 mg/kg eq for report PA-723-002.

In addition, green forage or green fodder samples from some trials (PA-723-002 to PA-723-004 and PA-723-007) were analysed for phorate (parent) and individual metabolites phorate sulfone, phorate sulfoxide, phoratoxon sulfoxide and phoratoxon sulfone (Roman, 1986: PA-730-067). Samples were analysed by GC-FPD following method M-1634. The reported LOQ was 0.05 mg/kg for parent, phorate sulfoxide, phorate sulfone, phoratoxon, phoratoxon sulfoxide, and phoratoxon sulfone. A method description and method validation report is not available and accuracy of residue concentrations is therefore unknown. It is not known if concentrations are expressed as mg/kg eq or as mg/kg for each metabolite individually.

Results are summarized in Table 52 (green sweet corn/maize plants). Recoveries were not verified for any of the compounds and therefore performance of the method at the time of sample analysis is unknown. In addition control samples were not analysed in report PA-723-002 and PA-723-004.

Table 38. Total phorate-related residues (oxidizable to phoratoxon sulfone) in sweet corn kernels plus cob (husk removed) from granular soil treatments at planting and/or during the growing season.

Location, year, (variety)	Form.	kg ai/ha	No	Method, timing	Soil	PHI, days	Total, mg/kg eq	Reference
Arlington, WI, USA, 1985, (Jubilee)	200 G	1.46	2	1st banded at planting (3 May) 2nd banded at cultivation, at 71-91 cm height (10 June)	silt loam pH = 6.0 4-5% om %clay ns	57	0.015	Higham, 1986 [PA-723-002]
Arlington, WI, USA, 1985, (Jubilee)	200 G	2.91	2	1st banded at planting (3 May) 2nd banded at cultivation, at 71-91 cm height (10 June)	silt loam pH = 6.0 4-5% om %clay ns	57	0.028	idem
Sanford, FL, USA, 1985 (Jubilee)	200 G	1.46	1	banded at planting (15 Sept)	sandy loam (details ns)	71	0.030	Higham, 1986 [PA-723-003]
Sanford, FL, USA, 1985 (Jubilee)	200 G	1.46	2	1st banded at planting (15 Sept) 2nd banded at cultivation at 91-122 cm height (19 Oct)	sandy loam (details ns)	37	0.016	Higham, 1986 [PA-723-004]
Sanford, FL, USA, 1985 (Jubilee)	200 G	2.91	2	1st banded at planting (15 Sept) 2nd banded at cultivation at 91-122 cm height (19 Oct)	sandy loam (details ns)	37	0.07; 0.11; mean 0.18 (a)	idem
Sanford, FL, USA, 1985 (Jubilee)	200 G	7.29	2	1st banded at planting (15 Sept) 2nd banded at cultivation at 91-122 cm height (19 Oct)	sandy loam (details ns)	37	0.20	idem
Corvallis, OR, USA, 1985 (Jubilee)	200 G	1.46	2	1st banded at planting (31 May) 2nd banded at cultivation, at 2-3 leaf stage (17 June)	sandy loam pH = 5.8 2.5% om %clay ns	74	< 0.01	Higham, 1986 [PA-723-007]
Corvallis, OR, USA, 1985 (Jubilee)	200 G	2.91	2	1st banded at planting (31 May) 2nd banded at	sandy loam pH = 5.8 2.5% om	74	< 0.01	idem

Location, year, (variety)	Form.	kg ai/ha	No	Method, timing	Soil	PHI, days	Total, mg/kg eq	Reference
				cultivation, at 2-3 leaf stage (17 June)	%clay ns			
Corvallis, OR, USA, 1985 (Jubilee)	200 G	7.29	2	1st banded at planting (31 May) 2nd banded at cultivation, at 2-3 leaf stage (17 June)	sandy loam pH = 5.8 2.5% om %clay ns	74	0.01	idem

a. Samples are assumed to be replicate field samples by present reviewer, therefore the mean value is calculated.

Legume Vegetables

Green beans

A total of 18 trials were conducted on green beans and green snap beans in the USA. Eight of the trials were conducted on green beans in 1985 and ten of the trials were conducted on snap beans in 1993. At planting, phorate granular formulation was either drilled to the side of the seed or banded over the row using a granular applicator at application rates of 1.68–4.70 kg ai/ha. Plot sizes were 56-190 m^2 with 76-91 cm row spacing. Commercially acceptable bean samples (2.3-3.2 kg whole pods) or green seeds (sample size not stated) were hand-harvested randomly 48 to 75 DAT. Residue data were also collected for bean plants (bean vines, bean forage). Results for these commodities are not summarized because the USA label prohibits the feeding of bean foliage treated with phorate to livestock and bean forage is not listed in the FAO manual as livestock feed. Samples were stored frozen at -20°C or lower for 6–10 months (storage period not indicated for reports 017 and 023, but maximum 390–397 d). This period is covered by the 2 year storage stability study in sugar beet tops or green maize forage/fodder. Total phorate-related residues (oxidizable to phoratoxon sulfone) were determined by GC-FPD (method M-1718). Reported LOQ was 0.05 mg/kg eq. This method is considered inaccurate for green beans (see methods section).

Results are summarised in Table 39 (green bean seeds without pods) and Table 40 (green seeds with pods). Samples were not corrected for concurrent method recoveries (70%–120% for pods with seeds, 79% for green seeds) nor for matrix interferences (< 0.3 LOQ in green bean pods or green bean seeds).

Table 39. Total phorate-related residues (oxidizable to phoratoxon sulfone) in green bean seeds (without pods) from granular soil treatments at planting.

Location; year; crop (variety)	Form.	kg ai/ha	no	Method; timing	Soil	PHI days	Total mg/kg eq	Reference
Jefferson, OR, USA; 1985; green beans (Blue Lake Bush)	200 G	2.35	1	banded over row; at planting (8 June)	silt loam; pH 5.9 3.1% om %clay ns	60	< 0.05	Higham, 1987, [PA-720-023]
Jefferson, OR, USA; 1985; green beans (Blue Lake Bush)	200 G	4.70	1	banded over row; at planting (8 June)	silt loam; pH 5.9 3.1% om %clay ns	60	< 0.05	idem
Jefferson, OR, USA; 1985; green beans (Blue Lake Bush)	200 G	2.35	1	drilled below seed; at planting (8 June)	silt loam; pH 5.9 3.1% om %clay ns	60	< 0.05	idem
Jefferson, OR, USA; 1985; green beans (Blue Lake Bush)	200 G	4.70	1	drilled below seed; at planting (8 June)	silt loam; pH 5.9 3.1% om %clay ns	60	0.06	idem

Table 40. Total phorate-related residues (oxidizable to phoratoxon sulfone) in green bean pods (with seeds) from granular soil treatments at planting.

Location; year; crop (variety)	Form.	kg ai/ha	no	Method; timing	Soil	PHI days	Total mg/kg eq	Reference
Corvallis, OR, USA; 1985; green beans (Blue Lake Bush)	200 G	2.35	1	banded over row; at planting (31 May)	sandy loam; pH 5.8 2.5% om %clay ns	75	< 0.05	Higham, 1987 [PA-720-017]
Corvallis, OR, USA; 1985; green beans (Blue Lake Bush)	200 G	4.70	1	banded over row; at planting (31 May)	sandy loam; pH 5.8 2.5% om %clay ns	75	< 0.05	idem
Corvallis, OR, USA; 1985; green beans (Blue Lake Bush)	200 G	2.35	1	drilled beside seed; at planting (31 May)	sandy loam; pH 5.8 2.5% om %clay ns	75	< 0.05	idem
Corvallis, OR, USA; 1985; green beans (Blue Lake Bush)	200 G	4.70	1	drilled beside seed; at planting (31 May)	sandy loam; pH 5.8 2.5% om %clay ns	75	< 0.05	idem
Hillsboro, OR, USA; 1993; snap beans (Oregon 91G)	200 G	2.24	1	side-dressed; at planting (25 June)	loam; pH 5.3 2.3% om 26% clay	52	≤ 0.05	Leonard, 1994 [PA-720-003]
Hillsboro, OR, USA; 1993; snap beans (Oregon 91G)	200 G	1.68	1	banded; at planting (25 June)	loam; pH 5.3 2.3% om 26% clay	52	≤ 0.05	idem
Waterloo, NY, USA; 1993; snap beans (Improved Tendergreen)	200 G	2.24	1	side-dressed; at planting (3 July)	sandy loam; pH 5.6 2.1% om 10% clay	50	≤ 0.05	Leonard, 1994 [PA-720-004]
Waterloo, NY, USA; 1993; snap beans (Improved Tendergreen)	200 G	1.68	1	banded; at planting (3 July)	sandy loam; pH 5.6 2.1% om 10% clay	50	≤ 0.05	idem
Conklin, MI, USA; 1993; snap beans (Provider)	200 G	2.24	1	side-dressed; at planting (12 June)	loam; pH 5.9 2.6% om 16% clay	48	≤ 0.05	Leonard, 1994 [PA-720-005]
Conklin, MI, USA; 1993; snap beans (Provider)	200 G	1.68	1	banded; at planting (12 June)	loam; pH 5.9 2.6% om 16% clay	48	≤ 0.05	idem
Delavan, WI, USA; 1993; snap beans (Strike)	200 G	2.24	1	side-dressed; at planting (16 July)	silt loam; pH 6.0 2.3% om 20% clay	54	≤ 0.05	Leonard, 1994 [PA-720-006]
Delavan, WI, USA; 1993; snap beans (Strike)	200 G	1.68	1	banded; at planting (16 July)	silt loam; pH 6.0 2.3% om 20% clay	54	≤ 0.05	idem
Belle glade, FL, USA; 1993; snap beans (Opus)	200 G	2.24	1	side-dressed; at planting (2 April)	peat/muck; pH 7.4 69.1% om; 13% clay	49	≤ 0.05	Leonard, 1994 [PA-720-007]
Belle glade, FL, USA; 1993; snap beans (Opus)	200 G	1.68	1	banded; at planting (2 April)	peat/muck; pH 7.4 69.1% om; 13% clay	49	≤ 0.05	idem

Pulses

Dry Beans

A total of 23 trials were conducted on dry harvested beans in the USA. Sixteen trials were conducted in 1985 and seven trials in 1990. Phorate granular formulation was applied at rates of 2.0 to 4.7 kg ai/ha in furrow, as a band over the row, or drilled to the side of the seed at planting. Plot sizes were 46-370 m^2 with 76–91 cm row spacing. Random samples of dry bean seeds were hand-harvested at 59 to 140 DAT (sample size not stated). Samples from some of the 1990 trials were allowed to dry for 0.5 – 6 d, and the dry seeds threshed using a stationary thresher. Residue data were also collected for dry bean hay (straw) samples. Results for these commodities are not summarized because the USA label prohibits the feeding of bean hay (straw) treated with phorate to livestock. Samples were stored frozen at -10 °C or lower for 94-191 d. The storage period was not stated for the 1985 trials, but is maximally 343 – 360 d. This period is covered by the 2-year storage stability study in dry beans. Total phorate-related residues (oxidizable to phoratoxon sulfone) were determined by GC-FPD (method M-1718 for 1985 trials or method M-1653 for 1990 trials). The reported LOQ was 0.05 mg/kg eq for each method. A validation report for method M-1653 is not available and accuracy of residue concentrations is therefore unknown.

Results are summarised in Table 41. Samples were not corrected for concurrent method recoveries (76%–133%) or for matrix interferences (< 0.3 LOQ to 0.018 mg/kg eq). The LOQ for report PA-720-010 and PA-720-011 was corrected to 0.016/0.3=0.06 mg/kg eq, because of matrix interferences.

Table 41. Total phorate-related residues (oxidizable to phoratoxon sulfone) in dry bean seeds from granular soil treatments at planting.

Location, year; crop (variety)	Form.	kg ai/ha	No	Method, timing	Soil	PHI, days	Total, mg/kg eq	Reference
Keeler, MI, USA; 1985; snap beans [a] (Tender Crop)	200 G	2.35	1	banded over row; at planting (16 July)	sandy loam; pH ns % om ns % clay ns	59	< 0.05	Higham, 1987 [PA-720-018]
Keeler, MI, USA; 1985; snap beans [a] (Tender Crop)	200 G	4.70	1	banded over row; at planting (16 July)	sandy loam; pH ns % om ns % clay ns	59	< 0.05	idem
Keeler, MI, USA; 1985; snap beans [a] (Tender Crop)	200 G	2.35	1	drilled beside seed; at planting (16 July)	sandy loam; pH ns % om ns % clay ns	59	< 0.05	idem
Keeler, MI, USA; 1985; snap beans [a] (Tender Crop)	200 G	4.70	1	drilled beside seed; at planting (16 July)	sandy loam; pH ns % om ns % clay ns	59	< 0.05	idem
Marcellus, MI, USA; 1985; snap beans [a] (Tender Crop)	200 G	2.35	1	banded over row; at planting (17 July)	sandy loam; pH ns 4.1% om % clay ns	60	< 0.05	Higham, 1987, [PA-720-021]
Marcellus, MI, USA; 1985; snap beans [a] (Tender Crop)	200 G	4.70	1	banded over row; at planting (17 July)	sandy loam; pH ns 4.1% om % clay ns	60	< 0.05	idem
Marcellus, MI, USA; 1985; snap beans [a] (Tender Crop)	200 G	2.35	1	drilled beside seed; at planting (17 July)	sandy loam; pH ns 4.1% om % clay ns	60	< 0.05	idem
Marcellus, MI, USA; 1985; snap beans [a]	200 G	4.70	1	drilled beside seed; at planting (17 July)	sandy loam; pH ns 4.1% om	60	< 0.05	idem

Location, year; crop (variety)	Form.	kg ai/ha	No	Method, timing	Soil	PHI, days	Total, mg/kg eq	Reference
(Tender Crop)					% clay ns			
East Lansing, MI, USA; 1985; dry beans (Seafarer)	200 G	2.35	1	Banded over row; at planting (5 June)	sandy clay loam; pH ns 1.6% om % clay ns	100	< 0.05	Higham, 1987 [PA-720-019]
East Lansing, MI, USA; 1985; dry beans (Seafarer)	200 G	4.70	1	Banded over row; at planting (5 June)	sandy clay loam; pH ns 1.6% om % clay ns	100	< 0.05	idem
East Lansing, MI, USA; 1985; dry beans (Seafarer)	200 G	2.35	1	In-furrow; at planting (5 June)	sandy clay loam; pH ns 1.6% om % clay ns	100	< 0.05	idem
East Lansing, MI, USA; 1985; dry beans (Seafarer)	200 G	4.70	1	In-furrow; at planting (5 June)	sandy clay loam; pH ns 1.6% om % clay ns	100	< 0.05	idem
Kimberley, ID, USA; 1985; dry beans (Viva Pink)	200 G	2.35	1	banded; at planting (11 June)	ns	111	< 0.05	Higham, 1987 [PA-720-022]
Kimberley, ID, USA; 1985; dry beans (Viva Pink)	200 G	4.70	1	banded; at planting (11 June)	ns	111	< 0.05	idem
Kimberley, ID, USA; 1985; dry beans (Viva Pink)	200 G	2.35	1	drilled; at planting (11 June)	ns	111	< 0.05	idem
Kimberley, ID, USA; 1985; dry beans (Viva Pink)	200 G	4.70	1	drilled; at planting (11 June)	ns	111	< 0.05	idem
Austin, CO, USA; 1990; dry beans (Othello)	200 G	2.02	1	knifed in-furrow; at planting (7 June)	silty loam pH 7.6 1.2% om 8% clay	97	< 0.05	Leonard, 1991 [PA-720-008]
Dixon, CA, USA; 1990; dry beans (Baby Lima)	200 G	2.29	1	knifed in-furrow at planting (18 May)	silty clay pH 6.8 2.5% om 40% clay	140	< 0.06	Leonard, 1991 Leonard, 1992 [PA-720-010]
Jerome, ID, USA; 1990 dry beans (Flamingo pink)	200 G	2.29	1	in-furrow; at planting (12 June)	silty loam pH 7.9 1.4% om 14% clay	95	< 0.06	Leonard, 1991 [PA-720-011]
York, NE, USA; 1990 navy beans (Chesmore)	200 G	2.29	1	drilled in furrow; at planting (28 May)	silty loam pH 6.1 2.7% om 26% clay	107	< 0.05	Leonard, 1991 [PA-720-012]
Northwood, ND, USA; 1990 pinto beans (Topaz)	200 G	2.29	1	drilled in furrow at planting (1 June)	silty loam pH 7.8 3.7% om 22% clay	98	< 0.05	Leonard, 1991 [PA-720-013]
Lamberton, MN, USA; 1990 navy beans (Snowflake)	200 G	2.29	1	drilled at planting (15 June)	clay loam pH 8.1 3.7% om 30% clay	123	< 0.05	Leonard, 1991 [PA-720-014]
Conklin, MI, USA;	200 G	2.29	1	drilled in-furrow	loam	92	< 0.05	Leonard, 1991

Location, year; crop (variety)	Form.	kg ai/ha	No	Method, timing	Soil	PHI, days	Total, mg/kg eq	Reference
1990 navy beans (Albron)				at planting (6 June)	pH 5.0 3.8% om 18% clay			[PA-720-015]

a because hay and seed samples were harvested on the same day, the reviewer assumed the seed samples to be dry. Confirmed by manufacturer.

Dry soya beans

Twenty eight trials were conducted in the USA in 1985 on soya beans. At planting, phorate granular formulation was applied as a side band in furrow, in a band, or drilled to the side of the seed, at rates of 1.1 to 9.4 kg ai/ha. Plot sizes were 3–240 m^2 with 76-96 cm row spacing. Dry soya bean seeds (sample size not stated) were harvested randomly from 132 to 146 DAT. Residue data was also collected for green plants and hay. Results for these commodities are not summarized because the USA label prohibits the feeding of soya bean foliage and hay treated with phorate to livestock. Samples were stored frozen at -20 °C or lower. The storage period was not indicated, but is maximally 159–173 d. This period is covered by a 2 year storage stability study in dry beans. Total phorate-related residues (oxidizable to phoratoxon sulfone) were determined by GC-FPD (method M-1653). The reported LOQ was 0.05 mg/kg eq. All samples were analysed on an as received basis.

Results are summarised in Table 42 below. Samples were not corrected for concurrent method recoveries (78%-97%) or for matrix interferences (< 0.3 LOQ).

Table 42. Total phorate-related residues (oxidizable to phoratoxon sulfone) in dry soya bean seeds [a] from granular soil treatments at planting.

Location, year, (variety)	Form.	kg ai/ha	No	Method; timing	Soil	PHI, days	Total, mg/kg eq	Reference
Bendena, KS, USA, 1985, (Pella)	200 G	2.35	1	in furrow; at planting (10 June)	clay loam pH ns 1.4% om %clay ns	142	< 0.05	Higham, 1987 [PA-720-009]
Bendena, KS, USA, 1985, (Pella)	200 G	4.70	1	in furrow; at planting (10 June)	clay loam pH ns 1.4% om %clay ns	142	< 0.05	idem
Bendena, KS, USA, 1985, (Pella)	200 G	2.35	1	banded; at planting (10 June)	clay loam pH ns 1.4% om %clay ns	142	< 0.05	idem
Bendena, KS, USA, 1985, (Pella)	200 G	4.7	1	banded; at planting (10 June)	clay loam pH ns 1.4% om %clay ns	142	< 0.05	idem
Scott, AR, USA; 1985, (Forrest)	200 G	1.10	1	In furrow; at planting (28 June)	sandy silt loam pH 6.4 0.8% om %clay ns	132	< 0.05	Higham, 1987 [PA-720-024]
Scott, AR, USA; 1985, (Forrest)	200 G	2.35	1	In furrow; at planting (28 June)	sandy silt loam pH 6.4 0.8% om %clay ns	132	< 0.05	idem
Scott, AR, USA; 1985, (Forrest)	200 G	3.36	1	In furrow; at planting (28 June)	sandy silt loam pH 6.4 0.8% om %clay ns	132	< 0.05	idem
Scott, AR, USA; 1985, (Forrest)	200 G	4.7	1	In furrow; at planting (28 June)	sandy silt loam pH 6.4 0.8% om	132	< 0.05	idem

Location, year, (variety)	Form.	kg ai/ha	No	Method; timing	Soil	PHI, days	Total, mg/kg eq	Reference
					%clay ns			
Scott, AR, USA; 1985, (Forrest)	200 G	9.4	1	In furrow; at planting (28 June)	sandy silt loam pH 6.4 0.8% om %clay ns	132	< 0.05	idem
Scott, AR, USA; 1985, (Forrest)	200 G	1.10	1	banded; at planting (28 June)	sandy silt loam pH 6.4 0.8% om %clay ns	132	< 0.05	idem
Scott, AR, USA; 1985, (Forrest)	200 G	2.35	1	banded; at planting (28 June)	sandy silt loam pH 6.4 0.8% om %clay ns	132	< 0.05	idem
Scott, AR, USA; 1985, (Forrest)	200 G	3.36	1	banded; at planting (28 June)	sandy silt loam pH 6.4 0.8% om %clay ns	132	< 0.05	idem
Scott, AR, USA; 1985, (Forrest)	200 G	4.7	1	banded; at planting (28 June)	sandy silt loam pH 6.4 0.8% om %clay ns	132	< 0.05	idem
Scott, AR, USA; 1985, (Forrest)	200 G	9.4	1	banded; at planting (28 June)	sandy silt loam pH 6.4 0.8% om %clay ns	132	< 0.05	idem
Hollandale, MN, USA; 1985, (Hardin)	200 G	4.7	1	banded; at planting (18 May)	loam pH 7.6 4.3% om %clay ns	146	< 0.05	Higham, 1987 [PA-720-025]
Hollandale, MN, USA; 1985, (Hardin)	200 G	9.4	1	banded; at planting (18 May)	loam pH 7.6 4.3% om %clay ns	146	< 0.05	idem
Hollandale, MN, USA; 1985, (Hardin)	200 G	4.7	1	drilled; at planting (18 May)	loam pH 7.6 4.3% om %clay ns	146	< 0.05	idem
Hollandale, MN, USA; 1985, (Hardin)	200 G	9.4	1	drilled; at planting (18 May)	loam pH 7.6 4.3% om %clay ns	146	< 0.05	idem
Glen Allen, MS, USA, 1985, (DPL 417)	200 G	1.1	1	banded; at planting (28 June)	silt loam pH 6.5 1.0% om % clay ns	138	< 0.05	Higham, 1987 [PA-720-026]
Glen Allen, MS, USA, 1985, (DPL 417)	200 G	2.35	1	banded; at planting (28 June)	silt loam pH 6.5 1.0% om % clay ns	138	< 0.05	idem
Glen Allen, MS, USA, 1985, (DPL 417)	200 G	3.36	1	banded; at planting (28 June)	silt loam pH 6.5 1.0% om % clay ns	138	< 0.05	idem
Glen Allen, MS, USA, 1985, (DPL 417)	200 G	4.7	1	banded; at planting (28 June)	silt loam pH 6.5 1.0% om % clay ns	138	< 0.05	idem
Glen Allen, MS, USA, 1985, (DPL 417)	200 G	9.4	1	banded; at planting (28 June)	silt loam pH 6.5 1.0% om % clay ns	138	< 0.05	idem
Glen Allen, MS, USA, 1985,	200 G	1.1	1	In furrow; at planting	silt loam pH 6.5	138	< 0.05	idem

Location, year, (variety)	Form.	kg ai/ha	No	Method; timing	Soil	PHI, days	Total, mg/kg eq	Reference
(DPL 417)				(28 June)	1.0% om % clay ns			
Glen Allen, MS, USA, 1985, (DPL 417)	200 G	2.35	1	In furrow; at planting (28 June)	silt loam pH 6.5 1.0% om % clay ns	138	< 0.05	idem
Glen Allen, MS, USA, 1985, (DPL 417)	200 G	3.36	1	In furrow; at planting (28 June)	silt loam pH 6.5 1.0% om % clay ns	138	< 0.05	idem
Glen Allen, MS, USA, 1985, (DPL 417)	200 G	4.7	1	In furrow; at planting (28 June)	silt loam pH 6.5 1.0% om % clay ns	138	< 0.05	idem
Glen Allen, MS, USA, 1985, (DPL 417)	200 G	9.4	1	In furrow; at planting (28 June)	silt loam pH 6.5 1.0% om % clay ns	138	< 0.05	idem

a because hay and seed samples were harvested on the same day, the reviewer assumed the seed samples to be dry. Confirmed by manufacturer.

Root and Tuber Vegetables

Potato

A total of 46 trials on potatoes were conducted in the USA and Canada. Twenty one trials were conducted in the USA in 1985, 1986, 1987, 1988, 1990, and 1991 and 25 trials were conducted in Canada in 1990. Phorate granular formulations were applied either in-furrow or in a band at planting, at rates of 2.19 to 266 kg ai/ha. In post-emergence trials, applications were made as a band or a side dressing at hilling, at rates of 2.7 to 10 kg ai/ha. Plot sizes were 3-474 m^2 with 81-96 cm row spacing. Random samples of potato tubers (2 to 5 kg) were collected before or at normal harvest time. For some studies, larger samples (45-91 kg) were collected (PA-724-013, PA-724-014). Adhering soil was brushed off the sampled tubers which were kept frozen at -20°C or lower for a period of 24 d up to 2.5 years. This period is covered by 2.5 year storage stability study on potato tubers. Total phorate-related residues (oxidizable to phoratoxon sulfone) were analysed by GC-FPD, following method M-1620 for the 1985 - 1988 USA trials or method M-1705 for the Canadian trials and the 1990-1991 USA trials. The reported LOQ for both methods was 0.05 mg/kg eq. No validation report is available for method M-1705 on raw potatoes and accuracy of residues values is unknown.

Phorate residue data on potato tubers is summarised in Table 43. Samples were not corrected for concurrent method recoveries (68%-119%) or for matrix interferences (< 0.3 LOQ for USA trials, <LOQ for Canadian trials). However, in a large number of Canadian trials control samples were not analysed and therefore performance of the method at the time of sample analysis is unknown. Because of matrix interferences, the LOQ for potatoes was increased to 0.032/0.3=0.1 mg/kg eq for study report PA-724-014. Further, recoveries were not verified in report PA-724-014, and therefore performance of the method at the time of sample analysis is unknown.

Table 43. Total phorate-related residues (oxidizable to phoratoxon sulfone) in potato tubers from granular soil treatments at planting or post-emergence.

Location, year, (variety)	Form.	kg ai/ha	No	Method, timing	Soil	PHI, days	Total mg/kg eq	Reference
Freeville, NY, USA; 1985, (Katahdin)	200 G	3.9	1	banded at planting (29 May)	silt loam (details ns)	104	<u>≤ 0.05</u>	Bohn, 1987 [PA-724-027]
Freeville, NY, USA; 1985,	200 G	8.0	1	banded at planting	silt loam (details ns)	104	0.06	idem

Location, year, (variety)	Form.	kg ai/ha	No	Method, timing	Soil	PHI, days	Total mg/kg eq	Reference
(Katahdin)				(29 May)				
Freeville, NY, USA; 1985, (Katahdin)	200 G	3.9	1	in-furrow at planting (29 May)	silt loam (details ns)	104	0.08	idem
Freeville, NY, USA; 1985, (Katahdin)	200 G	8.0	1	in-furrow at planting (29 May)	silt loam (details ns)	104	0.07	idem
Kimberly, ID, USA; 1985, (Russet)	200 G	3.9	1	in-furrow, at planting (1 May)	silt loam; pH 8.0 1.0% om %clay ns	142	≤ 0.05	Bohn, 1987 [PA-724-028]
Kimberly, ID, USA; 1985, (Russet)	200 G	8.0	1	in-furrow, at planting (1 May)	silt loam; pH 8.0 1.0% om %clay ns	142	< 0.05	idem
Kimberly, ID, USA; 1985, (Russet)	200 G	3.9	1	banded, at planting (1 May)	silt loam; pH 8.0 1.0% om %clay ns	142	≤ 0.05	idem
Kimberly, ID, USA, 1985, (Russet)	200 G	8.0	1	banded, at planting (1 May)	silt loam; pH 8.0 1.0% om %clay ns	142	< 0.05	idem
Jerome, ID, USA, 1986 (Russet Burbank)	200 G	3.92	1	in furrow, at planting (30 Apr)	sandy loam; pH 7.3 1.2% om %clay ns	95[b] 138	0.16 ≤ 0.05 (f)	Shimel, 1987 [PA-724-022]
Jerome, ID, USA, 1986 (Russet Burbank)	200 G	7.96	1	in furrow, at planting (30 Apr)	sandy loam; pH 7.3 1.2% om %clay ns	95[b] 138	< 0.05 < 0.05 (f)	idem
Jerome, ID, USA, 1987 (Russet Burbank)	200 G	7.96 3.92	2	1st in furrow, at planting (4 May) 2nd banded over hill (21 May, 17 d later)	sandy loam; pH 8.0 1.3% 10% clay	64[b]	< 0.1[a] (f) no recoveries	Devine and Green, 1990 [PA-724-014]
Jerome, ID, USA, 1987 (Russet Burbank)	200 G	7.96 3.92	2	1st modified in-furrow band at planting (4 May) 2nd banded over hill (21 May, 17 d later)	sandy loam; pH 8.0 1.3% 10% clay	64[b]	0.20[a] (f) no recoveries	idem
Hancock, WI, USA, 1987, (Russett Burbank)	200 G	6.7	1	in furrow, at planting (27 April)	sandy loam; pH 5.9-6.3 0.77% om 5% clay	77[b] 134	3.8 0.29	Dixon. and Gorrell, 1990, [PA-724-012]
Hancock, WI, USA, 1987, (Russett Burbank)	200 G	6.7	1	banded, at emergence at hilling (28 May)	sandy loam; pH 5.9-6.3 0.77% om 5% clay	77[b] 103	0.12[a] 0.08[a]	idem
Arlington, WI, USA; 1987, (Superior)	200 G	10	1	in furrow, at planting (7 May)	silt loam; pH 6.0 3.0% om 18% clay	77[b] 121	0.17[a] 0.50[a]	Dixon. and Gorrell, 1990, [PA-724-016]
Arlington, WI, USA; 1987, (Superior)	200 G	10	1	banded, at emergence at hilling	silt loam; pH 6.0 3.0% om	76[b] 108	< 0.05[a] < 0.05	idem

Location, year, (variety)	Form.	kg ai/ha	No	Method, timing	Soil	PHI, days	Total mg/kg eq	Reference
				(20 May)	18% clay			
Union Grove, WI, USA; 1988 (Russett Burbank)	200 G	2.7	1	side dressing at emergence at hilling (15 June)	clay; pH 7.2 5.6% om 46%clay	75^{b} 90^{b} 110	< 0.05 < 0.05 ≤ 0.05	Kleiner, 1990 [PA-724-017]
Rupert, ID, USA; 1988, (Russett Burbank)	200 G	2.6	1	side dressing at emergence at hilling (20 May)	sandy loam pH 7.6 1.2% om 8%clay	75^{b} 91^{b} 120	< 0.05 < 0.05 ≤ 0.05	Kleiner, 1990 [PA-724-018]
Northwood, ND; USA, 1990, (Norchip)	200 G	16.6	1	in furrow, at planting (17 May)	silt loam pH 7.9 4.1% om 20% clay	95	0.56^{a} (f)	Leonard, 1991, [PA-724-013]
Jerome, ID; USA, 1991, (Russet Burbank)	200 G	17.6	1	in furrow, at planting (2 May)	loam pH 8.1 1.5% om 14% clay	102^{b} 126	0.41 0.51, 0.76, 0.81, 0.92, 0.93, 1.0, 1.8, 2.1^{a}, 3.4^{a}, 5.1, mean 1.7 (f)	Leonard, 1992, [PA-724-009]
Northwood, ND; USA, 1991, (Norchip)	200 G	16.7	1	in furrow, at planting (28 May)	clay loam pH=7.9 4.1% om 32% clay	92^{b} 125	0.93 0.06^{a}, 0.18, 0.18^{a}, 0.26, 0.34, 0.39, 0.96, 1.1, 1.6, 1.8^{a}, mean 0.69 (f)	Leonard, 1992, [PA-724-008]
Cranford, Alberta, Canada; 1990 (Norchip)	150 G	222-266 (c)	1	in-furrow 1-7 d after planting (9 May)	sandy loam (details ns)	110 125	< 0.05 < 0.05	Dixon & Khunachak, 1990 [PA-724-015]
Lanoraie, Quebec, Canada; 1990 (Superior)	150 G	3.36	1	in-furrow at planting (8 May)	sand (details ns)	128	0.07 (no controls)	idem
St. Roch de l'Achigan; Quebec, Canada; 1990 (Kennebec)	150 G	3.36	1	in-furrow at planting (23 May)	sand (details ns)	124	0.15 (no controls)	idem
Chin, Alberta, Canada; 1990 (Russett Burbank)	150 G	2.33-2.89 (c)	1	in-furrow at planting (9 May)	sandy loam (details ns)	142	≤ 0.05 (no controls)	idem
Chin, Alberta, Canada; 1990 (Norchip)	150 G	2.33-2.89 (c)	1	in-furrow at planting (5 May)	sandy loam (details ns)	126	≤ 0.05 (no controls)	idem
Cloverdale, BC, Canada; 1990 (Norkotan Russett)	150 G	3.36	1	in-furrow at planting (27 May)	sandy clay loam (details ns)	123	≤ 0.05 (no controls)	idem
Cloverdale, BC, Canada; 1990 (Red La Soda)	150 G	3.36	1	in-furrow at planting (22 June)	sandy clay loam (details ns)	97	≤ 0.05 (no controls)	idem
Cloverdale, BC, Canada; 1990 (Yukon Gold)	150 G	3.36	1	in-furrow at planting (22 June)	sandy clay loam (details ns)	97	≤ 0.05 (no controls)	idem
Jacksonville, New Brunswick, Canada; 1990 (Russett Norkotan)	150 G	3.03	1	in-furrow at planting (10 May)	loam (details ns)	135	0.07 (no controls)	idem
York, Prince Edward Island, Canada; 1990 (Russett Burbank)	150 G	3.03	1	in-furrow at planting (29 May)	sandy loam (details ns)	132	≤ 0.05	idem
Woodstock, New Brunswick, Canada; 1990 (Russett Burbank)	150 G	3.03	1	in-furrow at planting (27 May^{d}) (16 May^{d})	clay loam (details ns)	118^{b} 129	< 0.05 ≤ 0.05	idem

Location, year, (variety)	Form.	kg ai/ha	No	Method, timing	Soil	PHI, days	Total mg/kg eq	Reference
Cornwall, Prince Edward Island, Canada; 1990 (Russett Burbank)	150 G	3.03	1	in-furrow at planting (2 June)	clay loam (details ns)	120	< 0.05	idem
Albany, Prince Edward Island, Canada; 1990 (Russett Burbank)	150 G	3.03	1	in-furrow at planting (10 June)	sandy loam (details ns)	125	0.16	idem
Centreville, Nova Scotia, Canada; 1990 (Somerset)	150 G	3.03	1	in-furrow at planting (28 May)	clay loam (details ns)	110	< 0.05 (no controls)	idem
Canning, Nova Scotia, Canada; 1990 (Superior)	150 G	3.36	1	in-furrow at planting (25 May)	sandy loam (details ns)	113	0.11	idem
Harrow, Ontario, Canada, 1990 (Superior)	150 G	2.78	1	in-furrow at planting (24 April)	sandy loam (details ns)	89	0.12	idem
St. François, Quebec, Canada; 1990 (Norland)	150 G	3.36	1	in-furrow at planting (16 May)	sand (details ns)	120	0.27 (no controls)	idem
Portage la Praire, Manitoba, Canada, 1990 (Norkotoh)	150 G	23-28 (c)	1	in-furrow at planting (30 May)	sandy loam (details ns)	92	< 0.05 (3) (e)	idem
Portage la Praire, Manitoba, Canada, 1990, (Shepody)	150 G	23-28 (c)	1	in-furrow at planting (30 May)	sandy loam (details ns)	92	< 0.05 (3) (e)	idem
Portage la Praire, Manitoba, Canada, 1990, (Norland)	150 G	23-28 (c)	1	in-furrow at planting (30 May)	sandy loam (details ns)	92	< 0.05 (2), 0.05 (e)	idem
Portage la Praire, Manitoba, Canada, 1990, (Russett)	150 G	23-28 (c)	1	in-furrow at planting (30 May)	sandy loam (details ns)	92	< 0.05, 0.09 [a], 0.10 [a] (e)	idem
Portage la Praire, Manitoba, Canada, 1990, (Russett)	150 G	2.19	1	in-furrow at planting (21 May)	sandy loam (details ns)	128	< 0.05 (2) (e)	idem
Portage la Praire, Manitoba, Canada, 1990, (Russett)	150 G	3.36	1	in-furrow at planting (21 May)	sandy loam (details ns)	128	< 0.05, 0.10 [a] (e)	idem
Shilo, Manitoba, Canada, 1990 (Norkotoh)	150 G	2.86	1	in-furrow at planting (10 May)	sandy loam (details ns)	110	< 0.05 (no controls)	idem
Portage la Praire, Manitoba, Canada, 1990, (Pontiac)	150 G	2.86	1	in-furrow at planting (10 May)	sandy loam (details ns)	133	< 0.05 (no controls)	idem

ns not stated
a Average from duplicate or triplicate analyses
b Sample obtained at earlier than normal harvest time
c In the study reports the application rate is indicated as kg product or kg active substance per unit length and row spacings are not indicated. The reviewer assumed a row spacing of 75-90 cm as listed in the Canadian GAP information, to calculate kg ai/ha dose rates. Exact dose rates are not known. Confirmed by manufacturer.
d Because location, variety and soil type is the same, the trials are considered as reversed residue trial: treatment on different days, but harvest on the same day.
e From the study report it is not clear if the values are the result of replicate plots or from replicate field samples. The reviewer assumes the results to come from replicate plots and therefore the individual values are listed without calculation of the mean.
f These samples were used in processing studies

Sugarbeets

A total of 16 trials on sugarbeets were conducted in the USA in 1985. Ten of these trials were carried out with one treatment either at planting or post-emergence. The rest of the trials used two applications, one at planting and the other post-emergence. Rates ranged from 1.68 to 3.36 kg ai/ha per application. Plot sizes ranged from 1000-20000 m^2 at row widths of 56-76 cm. Sugarbeet tops were collected randomly at several harvest intervals and roots were harvested randomly at maturity (30 to 149 d after the final application). Sample sizes were not stated. All samples were stored frozen at -20°C or lower. Storage time was not stated but was maximally 34-427 d. This period is covered by the 2 year storage stability study on sugarbeet roots and tops. Samples were analysed for total phorate-related residues (oxidizable to phoratoxon sulfone) by GC-FPD, following method M-1708. In study report PA-724-024, the method followed was M-1683. The reported LOQ for each of the methods was 0.05 mg/kg eq for sugarbeet tops and roots. All samples were analysed on an as received basis.

Phorate residue data are summarized in Table 44 (sugarbeet roots) and Table 56 (sugarbeet tops). Samples were not corrected for concurrent method recoveries (96%-122% for roots; 77%-109% for tops) or for matrix interferences (< 0.3 LOQ for roots; < 0.3 LOQ to 0.09 mg/kg eq for tops). Because of matrix interferences the valid LOQ for report PA-724-020 was increased to 0.023/0.3 = 0.08 mg/kg eq for sugarbeet tops. In study report PA-724-025 and report PA-724-026, high matrix interference (up to 0.09 mg/kg eq in PA-724-025 and up to 0.41 mg/kg eq in PA-724-026) were found for sugarbeets tops. In study report PA-724-024 concurrent method recoveries were not stated and therefore performance of the method at the time of sample analysis is unknown.

Table 44. Total phorate-related residues (oxidizable to phoratoxon sulfone) in sugarbeet roots from granular soil treatments at planting and/or post-emergence.

Location, year, (variety)	Form.	kg ai/ha	No	Method, timing	Soil	PHI, days	Parent mg/kg eq	Reference
Northwood, ND, USA 1985 (Bush Johnson 19)	200 G	1.68	1	by air, post-emergence foliar, (21 Aug: 85 d after planting)	silt loam pH ns 3.0-3.2% om % clay ns	30 32	< 0.05 < 0.05	Higham, 1987 [PA-724-020]
Northwood, ND, USA 1985 (Bush Johnson 19)	200 G	3.36	1	by air, post-emergence foliar, (21 Aug: 85 d after planting)	silt loam pH ns 3.0-3.2% om % clay ns	30 32	0.06 < 0.05	idem
Northwood, ND, USA 1985 (Bush Johnson 19)	200 G	1.68	2	1st in a band at planting (3 May); 2nd broadcast post emergence (22 Aug)	silt loam pH ns 3.0-3.2% om % clay ns	31	< 0.05	Higham, 1987 [PA-724-021]
Northwood, ND, USA 1985 (Bush Johnson 19)	200 G	3.36	2	1st in a band at planting (3 May); 2nd broadcast post-emergence (22 Aug)	silt loam pH ns 3.0-3.2% om % clay ns	31	< 0.05[a]	idem
Northwood, ND, USA 1985 (Bush Johnson 19)	200 G	1.68	2	1st in furrow at planting (3 May); 2nd broadcast post-emergence (22 Aug)	silt loam pH ns 3.0-3.2% om % clay ns	31	0.06	idem
Northwood, ND, USA 1985 (Bush Johnson 19)	200 G	3.36	2	1st in furrow at planting (3 May); 2nd broadcast post-emergence (22 Aug)	silt loam pH ns 3.0-3.2% om % clay ns	31	0.06	idem
Kimberly, ID, USA 1985 (WS 88)	200 G	1.68	1	drilled beside seed; at planting; (24 April)	silt loam pH 8.0 1.0% om % clay ns	149	< 0.05 (no recoveries)	Peterson, 1987 [PA-724-024]
Kimberly, ID, USA 1985 (WS 88)	200 G	3.36	1	drilled beside seed; at planting; (24 April)	silt loam pH 8.0 1.0% om	149	< 0.05 (no recoveries)	idem

Location, year, (variety)	Form.	kg ai/ha	No	Method, timing	Soil	PHI, days	Parent mg/kg eq	Reference
					% clay ns			
Kimberly, ID, USA 1985 (WS 88)	200 G	1.68	1	banded over the row at planting (24 April)	silt loam pH 8.0 1.0% om % clay ns	149	< 0.05 (no recoveries)	idem
Kimberly, ID, USA 1985 (WS 88)	200 G	3.36	1	banded over the row at planting (24 April)	silt loam pH 8.0 1.0% om % clay ns	149	< 0.05 (no recoveries)	idem
Kimberly, ID, USA 1985 (WS 88)	200 G	1.68	1	banded post emergence on foliage (11 June: 48 d after planting)	silt loam pH 8.0 1.0% om % clay ns	101	< 0.05 (no recoveries)	idem
Kimberly, ID, USA 1985 (WS 88)	200 G	3.36	1	banded post emergence on foliage (11 June: 48 d after planting)	silt loam pH 8.0 1.0% om % clay ns	101	< 0.05 (no recoveries)	idem
Mendota, CA, USA 1985 (SSE2)	200 G	1.68	2	1st in a band at planting (6 Mar); 2nd broadcast post-emergence; (22 May)	clay loam pH 8.2 1.0% om %clay ns	35	< 0.05	Higham, 1987 [PA-724-025]
Mendota, CA, USA 1985 (SSE2)	200 G	3.36	2	1st in a band at planting (6 Mar); 2nd broadcast post-emergence; (22 May)	clay loam pH 8.2 1.0% om %clay ns	35	< 0.05	idem
Mendota, CA, USA 1985 (SSE2)	200 G	1.68	1	by air, foliar post-emergence (22 May, 77 d after planting)	clay loam pH 8.2 1.0% om %clay ns	35	< 0.05	Higham, 1987 [PA-724-026]
Mendota, CA, USA 1985 (SSE2)	200 G	3.36	1	by air, foliar post-emergence (22 May, 77 d after planting)	clay loam pH 8.2 1.0% om %clay ns	35	< 0.05	idem

Cereal grains

Maize

A total of 45 trials were conducted on maize in 1971, 1981, 1985, 1986, 1990 and 1994 in various maize-growing areas of the USA. Phorate granular (GR) formulations were either applied as a single banded application at planting or as double or triple applications: one in a band at planting followed by either a side dress beside each row or a foliar treatment at cultivation. Rates per application ranged from 1.1 to 14.7 kg ai/ha.

Plot size was 23-530 m^2 at a row width of 76-97 cm. Random samples of maize grain and maize plants (immature with grains, mature without grains) were collected. Sampling details were not stated, except for the 1990 and 1994 maize trials in which the maize was shelled by hand or the plots were combined to obtain grain. The moisture content was 18% to 25%. Details on maize forage/fodder samples were not stated. Sample size was not stated, except for the 1985, 1990 and 1994 maize trials: 10-20 plants and 1.4-4.5 kg grain. Samples were stored frozen at -10°C or lower. Total storage time was not stated, but was maximally 9 to 266 d for most trials which is covered by the 24 month storage stability study on maize commodities. There is only one trial (PA-730-013) where maximum storage time of 761 d exceeds the verified storage stability period and accuracy of these residue values is unknown. Total phorate-related residues (oxidizable to phoratoxon sulfone) were determined by GC-FPD following method M-1618. A modification of method M-1618 was used in the 1986 and 1994 trials. For the 1994 trials no method validation report was available and therefore accuracy of the residue concentrations is unknown. Some trials followed Method M-1599

(PA-730-027, PA-730-029, PA-730-059, PA-730-061 and PA-730-062). The reported LOQ for each of the methods was 0.01 mg/kg eq for maize grains and 0.05 mg/kg eq for green maize forage and dry maize fodder. Due to matrix interferences and high recovery values, the LOQ for maize grain was increased to 0.02 mg/kg eq for all 1985 trials analyzed with method M-1618 (see methods section). The samples from the 1971 trials were analysed by GC-FPD method M-0455 and the 1981 samples were analysed by GC-FPD method M-0165. The reported LOQ for both methods was 0.05 mg/kg eq for maize grain and forage/fodder. A method validation report for method M-0165 was not available and accuracy of residue concentrations is therefore unknown. All samples were analysed on an as received basis.

Phorate residues in maize are summarised in Table 45 (maize grain) and Table 50 (green plants from maize) and Table 51 (dry plants from maize). Samples were not corrected for concurrent method recoveries (55%–125% for maize grain; 90% for green maize plants, 96%–102% for dry maize plants) nor for matrix interferences (< 0.3 LOQ for grain and plants). In report PA-730-010/-055/-056/-057/-058/-062 recoveries were not verified and therefore performance of the method at the time of sample analysis is unknown. Due to matrix interferences in control samples, the valid LOQ for grains was increased to 0.005/0.3=0.02 mg/kg eq for report PA-730-051 and 0.009/0.3=0.03 mg/kg eq for report PA-730-029.

In addition, green forage or green fodder samples from some trials (PA-730-055, PA-730-056) were analysed for phorate (parent) and individual metabolites phorate sulfone, phorate sulfoxide, phoratoxon sulfoxide and phoratoxon sulfone (Roman, 1986: PA-730-067). Samples were analyzed by GC-FPD following method M-1634. The reported LOQ was 0.05 mg/kg for parent, phorate sulfoxide, phorate sulfone, phoratoxon, phoratoxon sulfoxide, and phoratoxon sulfone. A method description and method validation report is not available and accuracy of residue concentrations is therefore unknown. It is not known if concentrations are expressed as mg/kg eq or as mg/kg for each metabolite individually.

Results are summarized in Table 52 (green maize plants). Recoveries were not verified for any of the compounds and therefore performance of the method at the time of sample analysis is unknown.

Table 45. Total phorate-related residues (oxidizable to phoratoxon sulfone) in maize grain from granular soil treatments at planting and/or during the growing season.

Location, year, (variety)	Form.	kg ai/ha	No	Method, timing	Soil	PHI, days	Total, mg/kg eq	Reference
Clinton, WI, USA, 1971 variety ns	150G	2.2	1	at planting (4 April)	ns	116	< 0.05	Peterson, 1973 [PA-730-013]
Clinton, WI, USA, 1971 variety ns	150G	4.4	1	at planting (4 April)	ns	116	< 0.05	idem
Ames, IA, USA, 1971 variety ns	150G	2.2	1	at planting (21 May)	ns	137	< 0.05	idem
Ames, IA, USA, 1971 variety ns	150G	4.4	1	at planting (21 May)	ns	137	< 0.05	idem
Ames, IA, USA, 1971 variety ns	150G	8.8	1	at planting (21 May)	ns	137	< 0.05	idem
Benedict, NE, USA, 1981, (Pioneer 3541)	150G	1.2	1	banded at cultivation, (9 June, 41 d after planting)	silt loam pH ns 2.8% om % clay ns	119	< 0.05 no recoveries	Higham, 1981 [PA-731-010]
Monticello, IL, USA; 1985 (T-1100)	200G	1.46	2	1st banded at planting (4 May) 2nd banded at	silt clay loam pH 5.8	30 134	< 0.01 < 0.01	Roman, 1986 [PA-730-059] [PA-730-061]

Location, year, (variety)	Form.	kg ai/ha	No	Method, timing	Soil	PHI, days	Total, mg/kg eq	Reference
				cultivation at layby (3 June) or after pollination, foliar (15 Sept)	6.1% om %clay ns			
Monticello, IL, USA; 1985 (T-1100)	200G	2.91	2	1st banded at planting (4 May) 2nd banded at cultivation at layby (3 June) or after pollination, foliar (15 Sept)	silt clay loam pH 5.8 6.1% om %clay ns	30 134	< 0.01 < 0.01	idem
Monticello, IL, USA; 1985 (T-1100)	200G	2.91 2.91 2.24	3	1st banded at planting (4 May) 2nd banded at cultivation at layby (3 June) 3rd after pollination, foliar (15 Sept)	silt clay loam pH 5.8 6.1% om %clay ns	30	0.036 no recoveries (d)	Roman, 1986 [PA-730-062]
Monticello, IL, USA; 1985 (T-1100)	200G	7.29 7.29 5.60	3	1st banded at planting (4 May) 2nd banded at cultivation at layby (3 June) 3rd after pollination, foliar (15 Sept)	silt clay loam pH 5.8 6.1% om %clay ns	30	0.076 no recoveries (d)	idem
Urbana, OH, USA, 1985 (Landmark CX733)	200G	1.46	2	1st banded at planting (24 April) 2nd side dress at cultivation at 76 cm height (4 June)	silt loam (details ns)	101	< 0.02	Higham, 1986 [PA-730-051]
Urbana, OH, USA, 1985 (Landmark CX733)	200G	2.91	2	1st banded at planting (24 April) 2nd side dress at cultivation at 76 cm height (4 June)	silt loam (details ns)	101	< 0.02	idem
York, NE, USA; 1985 (Pioneer 3377)	200G	2.91 2.91 2.24	3	1st banded at planting (4 May) 2nd banded at cultivation at 6-8 leaf stage (10 June) 3rd broadcast over the top at 2.1 m height (27 Aug)	silt loam pH ns 3.9% om %clay ns	29 44	< 0.02 < 0.02 no recoveries	Higham, 1986 [PA-730-066]
York, NE, USA; 1985 (Pioneer 3377)	200G	7.29 7.295.60	3	1st banded at planting (4 May) 2nd banded at cultivation at 6-8 leaf stage (10 June) 3rd broadcast over the top at 2.1 m height (27 Aug)	silt loam pH ns 3.9% om %clay ns	29 44	< 0.02 < 0.02 no recoveries	idem
York, NE, USA; 1985 (Pioneer 3377)	200G	1.46	2	1st banded at planting (21 May) 2nd banded at cultivation at 4-6 leaf stage (10 June)	silt loam pH ns 3.9% om %clay ns	106 121	< 0.02 < 0.02 no recoveries	Higham, 1986 [PA-730-055]
York, NE, USA; 1985 (Pioneer 3377)	200G	2.91	2	1st banded at planting (21 May) 2nd banded at cultivation at 4-6 leaf	silt loam pH ns 3.9% om %clay ns	106 121	< 0.02 < 0.02 no recoveries	idem

Location, year, (variety)	Form.	kg ai/ha	No	Method, timing	Soil	PHI, days	Total, mg/kg eq	Reference
				stage (10 June)				
York, NE, USA; 1985 (Pioneer 3377)	200G	1.46 1.12	2	1st banded at planting (21 May) 2nd broadcast over the top at 2.1 m height (26 Aug)	silt loam pH ns 3.9% om %clay ns	29 44	< 0.02 < 0.02 no recoveries	idem
York, NE, USA; 1985 (Pioneer 3377)	200G	2.91 2.24	2	1st banded at planting (21 May) 2nd broadcast over the top at 2.1 m height (26 Aug)	silt loam pH ns 3.9% om %clay ns	29 44	< 0.02 < 0.02 no recoveries	idem
York, NE, USA; 1985 (Pioneer 3377)	200G	1.46 1.12	2	1st banded at cultivation at 4-6 leaf stage (10 June) 2nd broadcast over the top at 2.1 m height (26 Aug)	silt loam pH ns 3.9% om %clay ns	29 44	< 0.02 < 0.02 no recoveries	idem
York, NE, USA; 1985 (Pioneer 3377)	200G	2.91 2.24	2	1st banded at cultivation at 4-6 leaf stage (10 June) 2nd broadcast over the top at 2.1 m height (26 Aug)	silt loam pH ns 3.9% om %clay ns	29 44	< 0.02 < 0.02 no recoveries	idem
York, NE, USA; 1985 (McCurdy 3784)	200G	1.46	2	1st banded at planting (4 May) 2nd banded at cultivation at 6-8 leaf stage (10 June)	silt loam pH ns 3.9% om %clay ns	107 122	< 0.02 < 0.02 no recoveries	Higham, 1986 [PA-730-056]
York, NE, USA; 1985 (McCurdy 3784)	200G	2.91	2	1st banded at planting (4 May) 2nd banded at cultivation at 6-8 leaf stage (10 June)	silt loam pH ns 3.9% om %clay ns	107 122	< 0.02 < 0.02 no recoveries	idem
York, NE, USA; 1985 (McCurdy 3784)	200G	1.46 1.12	2	1st banded at planting (4 May) 2nd broadcast over the top at 2.1 m height (26 Aug)	silt loam pH ns 3.9% om %clay ns	29 44	< 0.02 < 0.02 no recoveries	idem
York, NE, USA; 1985 (McCurdy 3784)	200G	2.91 2.24	2	1st banded at planting (4 May) 2nd broadcast over the top at 2.1 m height (26 Aug)	silt loam pH ns 3.9% om %clay ns	29 44	< 0.02 < 0.02 no recoveries	idem
York, NE, USA; 1985 (McCurdy 3784)	200G	1.46 1.12	2	1st banded at cultivation at 6-8 leaf stage (10 June) 2nd broadcast over the top at 2.1 m height (26 Aug)	silt loam pH ns 3.9% om %clay ns	29 44	< 0.02 < 0.02 no recoveries	idem
York, NE, USA; 1985 (McCurdy 3784)	200G	2.91 2.24	2	1st banded at cultivation at 6-8 leaf stage (10 June) 2nd broadcast over the top at 2.1 m height (26 Aug)	silt loam pH ns 3.9% om %clay ns	29 44	< 0.02 < 0.02 no recoveries	idem
Urbana, OH,	20OG	1.46	2	1st banded at planting	silt loam	35	< 0.02	Higham, 1986

Location, year, (variety)	Form.	kg ai/ha	No	Method, timing	Soil	PHI, days	Total, mg/kg eq	Reference
USA; 1985 (Landmark CX 733)				(24 April) 2nd broadcast at dough stage (9 Aug)	(details ns)		no recoveries	[PA-730-057]
Urbana, OH, USA; 1985 (Landmark CX 733)	200G	2.91	2	1st banded at planting (24 April) 2nd broadcast at dough stage (9 Aug)	silt loam (details ns)	35	< 0.02 no recoveries	idem
Champaign, IL, USA; 1985 (SP-240)	200G	1.12	2	1st banded at planting (22 April) 2nd banded at cultivation at 7 leaf stage (28 May) or after pollination, foliar (21 Aug)	silt loam pH ns 4.0% om %clay ns	30 115	< 0.02 < 0.02 no recoveries	Higham, 1986 [PA-730-058] [PA-730-060]
Champaign, IL, USA; 1985 (SP-240)		2.35	2	1st banded at planting (22 April) 2nd banded at cultivation at 7 leaf stage (28 May) or after pollination, foliar (21 Aug)	silt loam pH ns 4.0% om %clay ns	30 115	< 0.02 < 0.02 no recoveries	idem
New Holland, OH, USA, 1985 (GL 271)	200G	1.46	2	1st banded at planting (11 May) 2nd side dress at cultivation (20 June)	silty clay (details ns)	106	< 0.02	Higham, 1986 [PA-730-052]
New Holland, OH, USA, 1985 (GL 271)	200G	2.91	2	1st banded at planting (11 May) 2nd side dress at cultivation (20 June)	silty clay (details ns)	106	< 0.02	idem
Hollandale, MN, USA; 1985 (Pioneer 3803)	200G	1.46	2	1st banded at planting (18 May) 2nd banded at cultivation at 5 leaf stage (8 June)	sandy loam pH 7.5 4% om %clay ns	81 122	< 0.02 < 0.02	Higham, 1986 [PA-730-053]
Hollandale, MN, USA; 1985 (Pioneer 3803)	200G	1.46	2	1st banded at planting (18 May) 2nd broadcast over the top at 1.2 m height (20 July)	sandy loam pH 7.5 4% om %clay ns	30 39 80	< 0.02 < 0.02 < 0.02	idem
Hollandale, MN, USA; 1985 (Pioneer 3803)	200G	2.91	2	1st banded at planting (18 May) 2nd banded at cultivation at 5 leaf stage (8 June)	sandy loam pH 7.5 4% om %clay ns	81 122	< 0.02 no data	idem
Hollandale, MN, USA; 1985 (Pioneer 3803)	200G	2.91	2	1st banded at planting (18 May) 2nd broadcast over the top at 1.2 m height (20 July)	sandy loam pH 7.5 4% om %clay ns	30 39 80	< 0.02 < 0.02 < 0.02	idem
Monticello, IL, USA, 1986 (EK 7782)	136G[b]	1.12	1	banded at planting (16 May)	silt clay loam pH ns 4.2% om 28% clay	133	< 0.01	Higham and Fisher, 1988 [PA-730-031]
Monticello, IL, USA, 1986 (EK 7782)	143G[b]	1.12	1	banded at planting (16 May)	silt clay loam pH ns 4.2% om	133	< 0.01	idem

Location, year, (variety)	Form.	kg ai/ha	No	Method, timing	Soil	PHI, days	Total, mg/kg eq	Reference
					28% clay			
York, NE, USA, 1986 (Pioneer 3377)	136G [b]	1.12	1	banded at planting (19 May)	silt loam pH ns 3.7% om 22% clay	136	< 0.01	Higham and Fisher, 1988 [PA-730-032]
York, NE, USA, 1986 (Pioneer 3377)	143G [b]	1.12	1	banded at planting (19 May)	silt loam pH ns 3.7% om 22% clay	136	< 0.01	idem
York, NE, USA, 1986 (Pioneer 3377)	143G [b]	2.24	1	banded at planting (19 May)	silt loam pH ns 3.7% om 22% clay	136	< 0.01	idem
York, NE, USA, 1986 (Pioneer 3377)	143G [b]	5.60	1	banded at planting (19 May)	silt loam pH ns 3.7% om 22% clay	136	< 0.01[a]	idem
York, NE, USA; 1990 (Pioneer 3379)	200G	7.3	2	1st at planting (28 April) 2nd at cultivation (25 June)	silt clay loam pH 6.3 2.8% om 32% clay	86	< 0.01	Leonard, 1991 [PA-730-027]
Danville, IA, USA; 1990 (Dockendorf 7670)	200G	7.3	2	1st banded at planting (18 May) 2nd at cultivation at 7 leaf stage (2 July)	silt clay loam pH 5.9 3.9% om 34% clay	94 107	< 0.03 < 0.03	Leonard, 1991 [PA-730-029]
Webster City, IA, USA, 1994 (Land O'Lakes)	200G	14.7	2	1st banded at planting (17 May) 2nd banded at cultivation (25 July)	clay loam pH 5.8 4.4% om 30% clay	88	< 0.01	Leonard, 1995 [PA-730-068]

a. Result of duplicate analyses.
b. The 150 G product consists of two active ingredients with a ratio of 10:1 or 20:1 Thimet (phorate): Asana (esfenvalerate). This results in either 136 g phorate per kg product or 143 g phorate per kg product.
c. Results for these samples were presented in two different study reports. Although not stated, the reviewer assumes the samples to be replicate field samples and therefore the mean value was calculated. Only one of the samples was used for processing studies.
d. Samples from this trial were used in a processing study.

Sorghum

A total of 18 trials were conducted on sorghum in the USA in 1981, 1985, 1990, and 1993. Dose rates ranged from one application of granular phorate formulations at rates of 1.22-1.46 kg ai/ha at cultivation or at planting to 2 applications, one at planting and another at cultivation, at rates of 1.12 up to 7.3 kg ai/ha. Plot sizes ranged from 28 to 4050 m^2.

Random samples of grain or green fodder/forage were collected at normal harvest and in some cases 2 weeks before normal harvest (30 to 106 DAT). Samples were collected by hand or by combine. Sample sizes ranged from 25-35 grain heads and 10-12 plants for the 1985 trials to 2.2 to 100 kg of grain for the 1990 and 1993 trials. Sampling data for the 1981 trials are not available. Samples were stored frozen at unknown temperatures or at -20°C or lower. Although in most reports storage time was not indicated, the storage time will be maximally 33 to 406 d. This storage period is covered by the 2-year storage stability studies on maize commodities. Total phorate related residues (oxidizable to phoratoxon sulfone) were determined by GC-FPD, following Method M-1722. The 1981 trials followed a modified version of method C. The reported LOQ for both methods was 0.05 mg/kg eq for sorghum grain and forage/fodder. Method M-1722 is considered inaccurate for sorghum grain at all concentration levels and for green forage and dry fodder at concentrations below 0.2 mg/kg eq (see methods section). For method C no validation report is available and accuracy of the results is therefore unknown. All samples were analysed on an as received basis.

Phorate residues in sorghum are summarised in Table 46 (grain), Table 53 (green forage) and Table 54 (dry fodder). Samples were not corrected for concurrent method recoveries (77%-144% for grain; 95% -110% for forage/fodder) nor for matrix interferences (< 0.3 LOQ for grain and forage). In the 1981 trials, recoveries were not verified and therefore performance of the method at the time of sample analysis is unknown. Due to matrix interferences in control samples (up to 0.04 mg/kg eq), the valid LOQ for dry fodder in report PA-730-038 should be increased to an unacceptable level of 0.2 mg/kg eq. Therefore results for dry fodder from these trials must not be used for MRL derivation.

Table 46. Total phorate-related residues (oxidizable to phoratoxon sulfone) in sorghum grain from granular soil treatments at planting or at cultivation.

Location, year, (variety)	Form.	kg ai/ha	No	Method, timing	Soil	PHI, days	Total, mg/kg eq	Reference
Burlington, CO, USA, 1981, (Pioneer 8451)	150G	1.46	1	banded at cultivation, 35-41 cm height (6 July, 32 d after planting)	silt loam, pH 7.4 1.8% om 20% clay	95	< 0.05 no recoveries	Roman, 1982 [PA-731-006]
Waco, NE, USA, 1981, (Cargill 50)	150G	1.22	1	banded at cultivation, 20 cm height (16 June, 19 d after planting)	silt loam pH 6.6 4.0% om 12% clay	108	< 0.05 no recoveries	Bohn, 1982 [PA-730-063]
Wilbur, NE, USA, 1981, (GH H500B)	150G	1.22-1.46 [a]	1	banded at cultivation, 61 cm height (17 July, 56 d after planting)	silt loam pH 6.0 3.4% om 12% clay	76	< 0.05 no recoveries	Bohn, 1982 [PA-730-064]
Dorchester, NE, USA, 1981, (Mc Curdy 91)	200G	1.46	1	banded at cultivation, 56 cm height (17 July, 56 d after planting)	silt loam pH 5.9 2.3% om 21 clay	76	< 0.05 no recoveries	Bohn, 1982 [PA-730-065]
Dalhart, TX, USA, 1985, (Pioneer)	200G	1.46 1.12	2	1st banded at planting (27 May) 2nd by air, foliar (24 August)	sandy loam pH 7.3 0.5-1.0% om %clay ns	30 45	< 0.05 < 0.05[b]	Higham, 1987 [PA-730-035]
Dalhart, TX, USA, 1985, (Pioneer)	200G	2.91 2.24	2	1st banded at planting (27 May) 2nd by air, foliar (24 August)	sandy loam pH 7.3 0.5-1.0% om %clay ns	30 45	< 0.05 < 0.05	idem
Mt. Hope, KS, USA, 1985, (Dekalb DK 424)	200G	1.46 1.12	2	1st banded at planting (17 June) 2nd broadcast, foliar (18 August)	silt loam details ns	30 46	< 0.05 < 0.05	Higham, 1987 [PA-730-036]
Mt. Hope, KS, USA, 1985, (Dekalb DK 424)	200G	2.91 2.24	2	1st banded at planting (17 June) 2nd broadcast, foliar (18 August)	silt loam details ns	30 46	< 0.05 < 0.05	idem
Mt. Hope, KS, USA, 1985, (Dekalb DK 424)	200G	1.46 1.12	2	1st banded at planting (17 June) 2nd by air, foliar (18 August)	silt loam details ns	30 46	< 0.05 < 0.05	Higham, 1987 [PA-730-037]
Mt. Hope, KS, USA, 1985, (Dekalb DK 424)	200G	2.91 2.24	2	1st banded at planting (17 June) 2nd by air, foliar (18 August)	silt loam details ns	30 46	< 0.05 < 0.05	idem
Plainview, TX, USA, 1985, (PAG 4462)	200G	1.46 1.12	2	1st banded at planting (27 May) 2nd broadcast, foliar (7 Sept)	sandy clay loam pH ns 1.0-1.5% om % clay ns	30 44	< 0.05[b] < 0.05[b]	Higham, 1987 [PA-730-038]
Plainview, TX, USA, 1985, (PAG 4462)	200G	2.91 2.24	2	1st banded at planting (27 May) 2nd broadcast, foliar (7 Sept)	sandy clay loam pH ns 1.0-1.5% om % clay ns	30 44	< 0.05[b] < 0.05[b]	idem
Dodge City, KS, USA, 1990,	200G	7.3	2	1st banded at planting (25 May)	silt loam pH 7.0	93	< 0.05	Leonard, 1991 [PA-730-028]

Location, year, (variety)	Form.	kg ai/ha	No	Method, timing	Soil	PHI, days	Total, mg/kg eq	Reference
(Asgrow-Topaz)				2nd at cultivation, 10 leaf stage (10 July)	2.5% om 22% clay			
Lubbock, TX, USA, 1990, (Dekalb DK41Y)	200G	7.3	2	1st banded at planting (28 June) 2nd at cultivation, 10 leaf stage (8 Aug)	sandy loam pH 7.8 0.4% om 12% clay	99	< 0.05	Leonard, 1991 [PA-730-026]
York, NE, USA, 1993, (Northrup King)	200G	7.3	2	1st banded at planting (24 May) 2nd at cultivation, 91 cm height (31 July)	silt loam pH 4.9 2.9% om 22% clay	59	< 0.05	Leonard, 1994 [PA-730-022]
Snook, TX, USA, 1993, (DK 37)	200G	5.5	2	1st banded at planting (27 April) 2nd at cultivation, 8 leaf stage, 36-41 cm height (15 June)	silt loam pH 8.1 1.1% om 24% clay	60	< 0.05	Leonard, 1994 [PA-730-023]
Clarence, MO, USA, 1993, (Ciba-Geigy 251)	200G	7.3	2	1st banded at planting (16 June) 2nd at cultivation, 46-61 cm height (5 Aug)	silty clay loam pH 7.3 2.2% om 30% clay	60	< 0.05	Leonard, 1994 [PA-730-024]
Pratt, KS, USA, 1993, (Pioneer 8699)	200G	7.3	2	1st banded at planting (27 May) 2nd at cultivation, 40-50% headed, 61-76 cm height (27 July)	loam pH 6.3 2.1% om 20% clay	62	< 0.05	Leonard, 1994 [PA-730-025]

a. row spacing not stated, a row spacing of 30-36 inch was assumed by the present reviewer as in the other NE, 1981 trials.
b. average of two analyses

Oilseeds

Cottonseed

A total of 14 trials were conducted on cotton in the USA in 1985. Most trials were conducted with two applications at rates ranging from 0.84 to 7.17 kg ai/ha for the first application and 2.47 to 9.86 kg ai/ha for the second application. Plot size ranged from 37 to 565 m^2. Random samples of cotton seeds and dry fodder were collected. Sample sizes were not stated. Samples were stored frozen at -20°C or lower. Although storage time was not indicated, the storage time would be maximally 197 to 412 d. No storage studies have been carried out on cotton commodities (or other oilseeds) and therefore the accuracy of residue concentrations in cotton seeds is unknown. Storage stability for dry cotton fodder is covered by the 2 year storage stability study on dry maize fodder. Total phorate-related residues (oxidizable to phoratoxon sulfone) were determined by GC-FPD, following method M-1700. The reported LOQ was 0.05 mg/kg eq for cotton seed and dry fodder. However, because of high method recoveries, results below 1 mg/kg eq in cotton seed and dry fodder must be considered as inaccurate. All samples were analysed on an as received basis.

Phorate residues in cotton are summarised in Table 47 (seed) and Table 55 (dry fodder). Samples were not corrected for concurrent method recoveries (81%–112% for cotton seed, 125% for cotton plants) nor for matrix interferences (< 0.3 LOQ in seed, plant or dry plant).

Table 47. Total phorate-related residues (oxidizable to phoratoxon sulfone) in cotton seed from granular soil treatments at planting or at cultivation.

Location, year (variety)	Form.	kg ai/ha	No	Method, timing	Soil	PHI, days	Total, mg/kg eq	Reference
Glen Allen,	200 G	1.79	2	1st in furrow,	silt loam,	65	< 0.05	Higham, 1987

Location, year (variety)	Form.	kg ai/ha	No	Method, timing	Soil	PHI, days	Total, mg/kg eq	Reference
MS, USA, 1985 (DPL 41)		2.47		at planting 7 May 2nd side-dressed 10 July	pH 6.8 1.0% om %clay ns			[PA-750-005]
Glen Allen, MS, USA, 1985 (DPL 41)	200 G	2.47 4.93	2	1st in furrow, at planting 7 May 2nd side-dressed 10 July	silt loam, pH 6.8 1.0% om %clay ns	65	< 0.05	idem
Glen Allen, MS, USA, 1985 (DPL 41)	200 G	3.59 4.93	2	1st in furrow, at planting 7 May 2nd side-dressed 10 July	silt loam, pH 6.8 1.0% om %clay ns	65	< 0.05	idem
Glen Allen, MS, USA, 1985 (DPL 41)	200 G	7.17 9.86	2	1st in furrow, at planting 7 May 2nd side-dressed 10 July	silt loam, pH 6.8 1.0% om %clay ns	65	< 0.05[a]	idem
Plainview, TX, USA 1985 (Paymaster)	200 G	1.79 2.47	2	1st in furrow, at planting 31 May 2nd side-dressed 14 Sept	clay loam pH 7.5 1.5% om %clay ns	64	< 0.05	Higham, 1987 [PA-750-006]
Plainview, TX, USA 1985 (Paymaster)	200 G	3.59 4.93	2	1st in furrow, at planting 31 May 2nd side-dressed 14 Sept	clay loam pH 7.5 1.5% om %clay ns	64	< 0.05	idem
Tulare, CA, USA 1985 (Acala)	200 G	1.79 2.47	2	1st in furrow, at planting 11 April 2nd side-dressed 3 June	sand loam pH ns 1.0% om %clay ns	120	< 0.05	Higham, 1987 [PA-750-007]
Tulare, CA, USA 1985 (Acala)	200 G	3.59 4.93	2	1st in furrow, at planting 11 April 2nd side-dressed 3 June	sand loam pH ns 1.0% om %clay ns	120	< 0.05[a]	idem
Belle Mina, AL, USA 1985 (DPL 50)	200 G	0.84	1	in furrow, at planting 19 April	ns	137	< 0.05	Higham, 1987 [PA-750-008]
Belle Mina, AL, USA 1985 (DPL 50)	200 G	1.79 2.47	2	1st in furrow, at planting 19 April 2nd side-dressed 5 June	ns	90	< 0.05	idem
Belle Mina, AL, USA 1985 (DPL 50)	200 G	3.59 4.93	2	1st in furrow, at planting 19 April 2nd side-dressed 5 June	ns	90	< 0.05[a]	idem
Dysart, AZ, USA 1985 (DPL 90)	200 G	1.79 3.59	2	1st in furrow, at planting 1 May 2nd side-dressed 27 August	ns	61	< 0.05	Higham, 1987 [PA-750-009]
Dysart, AZ, USA 1985 (DPL 90)	200 G	2.47 4.93	2	1st in furrow, at planting 1 May 2nd side-dressed 27 August	ns	61	< 0.05 (2), mean < 0.05[b]	idem

Location, year (variety)	Form.	kg ai/ha	No	Method, timing	Soil	PHI, days	Total, mg/kg eq	Reference
Dysart, AZ, USA 1985 (DPL 90)	200 G	7.17 9.86	2	1st in furrow, at planting 1 May 2nd side-dressed 27 August	ns	61	< 0.05	idem

a Average of two analyses

b Present reviewer assumes that results come from replicate field samples, therefore the mean value is calculated.

In addition in two earlier studies, residues were analysed for cotton leaves at various timepoints.

In the first study, cotton seeds, variety Ashmouni, were planted in the field in Egypt on March 15, 1962 (Zaki and El-Sayed, 1968: PA-905-048). Plot size was 5 rows of 4.5 m. During the growing season, cotton plants were sprayed three times with an EC formulation of unlabelled phorate with a spray concentration of 0.1 kg ai/hL at 15 day intervals. Plants were sprayed with a knapsack sprayer, low volume type. First application was on 29 July, 1962. Sprayed cotton leaves without stems, avoiding new growth, were collected one hr after each spraying event and then 1, 3, 6, 9, 12 and 15 days after treatment. After the final spray, cotton leaves were collected after 1 and 24 hrs and then at weekly intervals up to the fourth week following after treatment. Storage conditions were not stated.

Both sides of the leaves were washed with distilled water (pH =7). Washed leaves were homogenised with water and filtered. Total phorate-related residues were determined by their acetylcholinesterase inhibitive power in an electrometric acetylcholinesterase assay, Method A. This method is considered inaccurate (see methods section).

One hour after the first spray, 65% of the initial phorate residues had penetrated into the leaf tissues. Penetrated and surface residues reached a maximum value of 4.0-4.5 mg/kg eq 1 DAT. Thereafter, both the surface and penetrated residues tended to decrease gradually over the 15 day or 4 week period.

In the second study, cotton seeds, variety Ashmouni, were planted in the field in Egypt in 1963 (Zaki and El-Sayed, 1968: PA-905-048). During the growing season, cotton plants were sprayed twice with a mixture of Endrin and DDT/lindane and five times with an EC formulation of unlabelled phorate with a spray concentration of 0.075 kg ai/hL at 15 day intervals. Plants were sprayed with a knapsack sprayer, high volume type. The first phorate application was made on 27 July, 1963. Foliage (sprayed leaves, growing points - tops) was collected 1, 3, 6 hrs after the first spraying and then after 1, 3, 6, 9, 12 and 15 days. Samples from successive spray events were not analysed. Storage conditions were not stated.

Both sides of the leaves were washed with distilled water (pH =7). Washed leaves were homogenised with water and filtered. Aqueous extracts were extracted with chloroform. Total phorate-related residues in water and chloroform layers were determined by their acetylcholinesterase inhibitive power in an electrometric acetylcholinesterase assay, Method A. This method is considered inaccurate (see methods section). Chloroform extracts were subjected to paper chromatography (no details submitted).

One hour after the first spray, 73% of the initial phorate residues had penetrated into the leaf tissues. At this timepoint, four compounds could be found in the surface leaf and leaf tissue chloroform extracts: parent, phorate sulfoxide, phorate sulfone, and phoratoxon sulfone. In the surface leaf extracts, parent and phorate sulfoxide were not be found at later timepoints, while phorate sulfone and phoratoxon sulfone were found on the leaf surface 3 and 6 hours and 1, 3 days after treatment. Leaf tissue chloroform extracts contained all four compounds during the 15 day period after application. In addition, leaf tissue chloroform extracts contained phoratoxon and an unknown compound at DAT 9, 12 and 15.

The tops of the plants, 15 DAT, contained 0.08 mg/kg eq as hydrolysed products (water layer) and 0.09 mg/kg eq as active metabolites (chloroform layer), which were ascribed to phoratoxon sulfone and an unknown compound.

Seed for Beverages

Coffee Beans

A total of 19 trials on coffee were conducted, 2 in Colombia, 13 in Brazil, and 4 in Puerto Rico.

In the trials in Colombia a plot size of ten 3-year old plants was used. Ripe berries were picked by hand, de-pulped and sun-dried in the normal commercial manner for an unstated period. Sample sizes were not stated. The moisture content of the beans ranged from 8.6-9.6% at 62 d and 7.3%-8.8% at 90 d. The dry unroasted coffee beans were stored frozen (temperature not stated).

In seven trials in Brazil a plot size of 3-8 hills, corresponding to 6-16 4-year old trees was used. Harvested coffee beans were sun-dried and shelled (husked) for an unstated period. Sample size was not stated. Dry unroasted coffee beans (green beans) were stored between 15-25 °C.

In addition four trials in Brazil were carried out at exaggerated dose rates on 21-year old trees for processing studies. Harvested coffee beans were airs dried for a period of 21 d. Sample sizes were not stated. Dry unroasted coffee beans (green beans) were stored frozen (temperature not stated).

In the trials in Puerto Rico a plot size of 10-14 trees was used. Harvested berries were de-pulped and placed in a fabric bag to ferment for 14-24 hrs. Sample sizes were not stated. Thereafter, beans were washed leaving the fermenting liquor and berries in the bag for another 24 hrs (only in trials PA-790-017). Thereafter, beans were washed, dried and stored at room temperature (temperature not stated).

The storage period is not stated in any of the study reports but is maximally 4-12 months (ambient or frozen). No storage studies have been carried out on coffee, and therefore the accuracy of residue concentrations is unknown.

The beans were analysed for total phorate-related residues (oxidizable to phoratoxon sulfone) by GC-FPD, following method M-684. The samples from the 1975 trials were analysed by GC-AFID. The reported LOQ was 0.05 mg/kg eq, except for the 1983 trials (0.02 mg/kg eq). No method validation report is available and accuracy of residue concentrations is therefore unknown.

Phorate residue data on coffee beans from trials in Colombia, Brazil, and Puerto Rico are summarised in Table 47. Samples were not corrected for concurrent method recoveries (84%) or for matrix interferences (< 0.3 LOQ, except for the 1983 Brazilian trials). In the 1975 Columbian trials and 1978 Brazilian and Puerto Rican trials and 1983 Brazilian trials, recoveries were not verified and therefore performance of the method at the time of sample analysis is unknown. Matrix interferences from control samples were not verified in the 1978 Brazilian trials. Because of matrix interferences, the LOQ was increased to 0.008/0.3=0.03 mg/kg eq, in the 1983 Brazilian trials.

Table 47. Phorate residues in dried coffee beans from granular soil treatments around the trees.

Location, year (variety)	Form.	Dose rate	No	Method, timing	Soil	PHI, days	Parent, mg/kg eq	Reference
Caldas, Colombia 1975, (ns)	50 G	2.7 kg ai/ha [a] (3.0 g ai/tree) (3 year old)	1	5-10 cm deep circular furrow under plant canopy, August	ns	62 90	< 0.05 < 0.05 no recovery	Manuel and Whitney, 1976 [PA-790-013]
Caldas,	50 G	5.3 kg ai/ha [a]	1	5-10 cm deep	ns	62	< 0.05	idem

Location, year (variety)	Form.	Dose rate	No	Method, timing	Soil	PHI, days	Parent, mg/kg eq	Reference
Colombia 1975, (ns)		(6.0 g ai/tree) (3 year old)		circular furrow under plant canopy, August		90	<u>≤ 0.05</u> no recovery	
Cafelandia, Brazil 1976-1977, (Mundo Novo)	100 G	2.0 kg ai/ha [c] (2.0 g ai/tree) (4 year old)	1	in furrows on each side of the trees, 11 Nov	ns	231	< 0.05	Elenewski and Whitney, 1978 [PA-790-014]
Cafelandia, Brazil 1976-1977, (Mundo Novo)	100 G	2.0 kg ai/ha [c] (2.0 g ai/tree) (4 year old)	2	in furrows on each side of the trees, 11 Nov and 3 March	ns	129	< 0.05	idem
Cafelandia, Brazil 1976-1977, (Mundo Novo)	830 LC	1.7 kg ai/ha [c] (1.7 g ai/tree)[b] (4 year old)	1	in furrows on each side of the trees, 11 Nov	ns	231	< 0.05	idem
Cafelandia, Brazil 1976-1977, (Mundo Novo)	830 LC	1.7 kg ai/ha [c] (1.7 g ai/tree)[b] (4 year old)	2	in furrows on each side of the trees, 11 Nov and 3 March	ns	129	< 0.05	idem
Guaranta, Brazil 1976-1977, (Mundo Novo)	830 LC	1.7 kg ai/ha [c] (1.7 g ai/tree)[b] (4 year old)	3	spray at the base of the tree trunk 11 June to 17 Sept	ns	106	< 0.05	Elenewski and Whitney, 1978 [PA-790-015]
Jau, Brazil 1976-1977, (ns)	100 G	2.0 kg ai/ha [c] (2.0 g ai/tree) (4 year old)	2	in furrows on each side of the trees, 15 Oct and 2 March	ns	105	< 0.05	Elenewski and Whitney, 1978 [PA-790-016]
Pindorama, Sitio Gramado, Brazil, 1978, (ns)	100 G	2 kg ai/ha (2.0 g ai/tree) (age ns)	1	Soil treatment 24 Feb	ns	123	< 0.05 no recovery no controls	Bohn and Rose, 1979 [PA-790-019]
Pindorama, Sitio Gramado, Brazil, 1978, (ns)	100 G	4 kg ai/ha (4.0 g ai/tree) (age ns)	1	Soil treatment 24 Feb	ns	123	< 0.05 no recovery no controls	idem
Pindorama, Sitio Gramado, Brazil, 1978, (ns)	100 G	6 kg ai/ha (6.0 g ai/tree) (age ns)	1	Soil treatment 24 Feb	ns	123	< 0.05 no recovery no controls	idem
Paulinia, Sao Paulo, Brazil, 1983 (Mundo novo)	50 G	8 kg ai/ha [c] (8.0 g ai/tree) (21 yr old)	1	Soil treatment from trunk to drip line 4 Jan	ns	160	< 0.03 no recovery	Babbitt and Lesiewicz, 1984 [PA-790-023]
Paulinia, Sao Paulo, Brazil, 1983 (Mundo novo)	50 G	16 kg ai/ha [c] (16 g ai/tree) (21 yr old)	1	Soil treatment from trunk to drip line 4 Jan	ns	160	< 0.03 no recovery	idem
Paulinia, Sao Paulo, Brazil, 1983 (Mundo novo)	50 G	40 kg ai/ha [c] (40 g ai/tree) (21 yr old)	1	Soil treatment from trunk to drip line 4 Jan	ns	160	0.057 no recovery	idem
Paulinia, Sao Paulo, Brazil, 1983 (Mundo novo)	50 G	80 kg ai/ha [c] (80 g ai/tree) (21 yr old)	1	Soil treatment from trunk to drip line 4 Jan	ns	160	0.48 no recovery	idem
Lares,	150 G	4 kg ai/ha [d]	1	Soil treatment	ns	120	< 0.05	Bohn and Rose, 1979

Location, year (variety)	Form.	Dose rate	No	Method, timing	Soil	PHI, days	Parent, mg/kg eq	Reference
Puerto Rico, 1978, (Caturra)		(1.3 g ai/m tree height) (age ns)		at base of the tree, 6 July		153	< 0.05 no recovery no controls	[PA-790-017]
Lares, Puerto Rico, 1978, (Caturra)	150 G	8 kg ai/ha [d] (2.6 g ai/m tree height) (age ns)	1	Soil treatment at base of the tree, 6 July	ns	120 153	< 0.05 < 0.05 no recovery no controls	idem
Adjuntas, Puerto Rico, 1978	150 G	4 kg ai/ha [d] (1.3 g ai/m tree height) (age ns)	1	Soil treatment at base of the tree, 11 May	ns	96 134	≤ 0.05 < 0.05 no recovery no controls	Bohn and Rose, 1979 [PA-790-018]
Adjuntas, Puerto Rico, 1978	150 G	8 kg ai/ha [d] (2.6 g ai/m tree height) (age ns)	1	Soil treatment at base of the tree, 11 May	ns	96 134	≤ 0.05 < 0.05 no recovery no controls	idem

a. The dose rate is only given as g ai/tree. One 3-year old tree is 11.25 m^2 as stated in the study report and therefore the dose rate is calculated from (3.0 - 6.0 g ai/tree / 11.25 m^2) x 10 (in kg ai/ha).

b. The LC-8 formulation contains 830 g ai/L and an amount of 4.0 ml is used per hill (2 trees/hill). Therefore an amount of 2.0 x 830/1000 = 1.66 g ai/tree is used here. The manufacturer used a value of 1.9 g ai/tree.

c. The dose rate is only given as g ai/tree. Based on the Brazilian label, an amount of 1660 trees per hectare is used to decide between a dose rate as g/tree (≤ 1660 trees/ha) or kg ai/ha (> 1660 trees/ha). The manufacturer used a value of 1660 trees/ha to calculate the dose rate as: 1.9-2.0 (g ai/tree) x 1660 (trees/ha) / 1000 = 3.2-3.3 kg ai/ha. This value does not correspond with the value of 2-4-6 kg ai/ha for a dose rate of 2.0-4.0-6.0 g ai/tree as given in 1978 trials. The value in the 1978 trials corresponds with a value of 10 m^2 per tree, which is close to the value in the 1975 Colombian trial. Because present day practices are not necessarily applicable to cultivation practices in the past, the present reviewer calculated dose rates from the assumption that 1 tree is 10 m^2 using the formula: [1.66-2.0 (g ai/tree) / 10 (m^2)] x 10 = 1.7 - 2.0 kg ai/ha.

d. The dose rate is only given as 0.4-0.8 g ai/ft tree height (=1.3-2.6 g ai/m tree height). According to the manufacturer, on average 4-5 years after cultivation, coffee trees are pruned to maintain a height of about 10 ft (3.05 m), for ease of harvest of berries. Based on the Brazilian label, an amount of 1660 trees per hectare is used to decide between a dose rate as g/tree (≤ 1660 trees/ha) or kg ai/ha (> 1660 trees/ha). The manufacturer used a value of 1660 trees/ha to calculate the dose rate as: 0.4-0.8 (g ai/ft tree height) x 10 (ft) x 1660 (trees/ha) / 1000 = 6.6 - 13 kg ai/ha. As indicated in legend b, the present reviewer prefers a tree surface of 10 m^2 per tree, and calculates the dose rate from: [0.4-0.8 (g ai/ft tree height) x 10 (ft) / 10 (m^2)] x 10 = 4 - 8 kg ai/ha.

Straw, fodder and forage of cereal grains and grasses

For description of trials, see primary crop

Table 49. Total phorate-related residues (oxidizable to phoratoxon sulfone) in sweet corn plants (forage/fodder) from granular soil treatments at planting or at cultivation.

Location, year, crop, (variety)	Form.	kg ai/ha	No	Method, timing	Soil	PHI, days	Total, mg/kg eq	Reference
Arlington, WI, USA, 1985, sweet corn (Jubilee)	200G	1.46	2	1st banded at planting (3 May) 2nd banded at cultivation, at 71-91 cm height (10 June)	silt loam pH = 6.0 4-5% om %clay ns	28 [a] 57 [b]	< 0.06 < 0.06	Higham, 1986 [PA-723-002]
Arlington, WI, USA, 1985, sweet corn (Jubilee)	200G	2.91	2	1st banded at planting (3 May) 2nd banded at cultivation, at 71-91 cm height (10 June)	silt loam pH = 6.0 4-5% om %clay ns	28 [a] 57 [b]	< 0.06 0.11	idem

Location, year, crop, (variety)	Form.	kg ai/ha	No	Method, timing	Soil	PHI, days	Total, mg/kg eq	Reference
Sanford, FL, USA, 1985 sweet corn (Jubilee)	200G	1.46	1	banded at planting (15 Sept)	sandy loam (details ns)	71 [b]	0.15 (no controls)	Higham, 1986 [PA-723-003]
Sanford, FL, USA, 1985 sweet corn (Jubilee)	200G	1.46	2	1st banded at planting (15 Sept) 2nd banded at cultivation at 91-122 cm height (19 Oct)	sandy loam (details ns)	37 [b]	0.09	Higham, 1986 [PA-723-004]
Sanford, FL, USA, 1985 sweet corn (Jubilee)	200G	2.91	2	1st banded at planting (15 Sept) 2nd banded at cultivation at 91-122 cm height (19 Oct)	sandy loam (details ns)	37 [b]	0.93, 1.6; mean 1.3 [d]	idem
Sanford, FL, USA, 1985 sweet corn (Jubilee)	200G	7.29	2	1st banded at planting (15 Sept) 2nd banded at cultivation at 91-122 cm height (19 Oct)	sandy loam (details ns)	37 [b]	2.1	idem
Corvallis, OR, USA, 1985 sweet corn (Jubilee)	200G	1.46	2	1st banded at planting (31 May) 2nd banded at cultivation, at 2-3 leaf stage (17 June)	sandy loam pH = 5.8 2.5% om %clay ns	29 [a] 45 [a] 59 [a] 74 [b]	0.10 < 0.05 < 0.05 < 0.05	Higham, 1986 [PA-723-007]
Corvallis, OR, USA, 1985 sweet corn (Jubilee)	200G	2.91	2	1st banded at planting (31 May) 2nd banded at cultivation, at 2-3 leaf stage (17 June)	sandy loam pH = 5.8 2.5% om %clay ns	29 [a] 45 [a] 59 [a] 74 [b]	0.35 0.06 0.08 < 0.05	idem
Corvallis, OR, USA, 1985 sweet corn (Jubilee)	200G	7.29	2	1st banded at planting (31 May) 2nd banded at cultivation, at 2-3 leaf stage (17 June)	sandy loam pH = 5.8 2.5% om %clay ns	29 [a] 45 [a] 59 [a] 74 [b]	0.98 0.09 0.29 0.05	idem

a Green forage. Maize plant harvested before normal harvest time. The reviewer assumes that this is the whole plant with immature grains and therefore the plant is still green.

b Green fodder. Maize plant harvested at the same time as sweet corn cobs. The reviewer assumes that this is the plant without corn cobs. Based on commercial practices, plants are harvested green. Confirmed by manufacturer.

c Samples are assumed to be replicate field samples by the present reviewer, therefore the mean value is calculated.

Table 50. Total phorate-related residues (oxidizable to phoratoxon sulfone) in green maize plants (forage) from granular soil treatments at planting or at cultivation.

Location, year, crop, (variety)	Form.	kg ai/ha	No	Method, timing	Soil	PHI, days	Total, mg/kg eq	Reference
Clinton, WI, USA, 1971 maize, (variety ns)	150G	2.2	1	at planting (4 April)	ns	98[a]	< 0.05	Peterson, 1973 [PA-730-013]
Clinton, WI, USA, 1971 maize, (variety ns)	150G	4.4	1	at planting (4 April)	ns	98[a]	< 0.05	idem
Ames, IA, USA, 1971 maize, (variety ns)	150G	2.2	1	at planting (21 May)	ns	83[a] 103[a]	< 0.05 < 0.05	idem
Ames, IA, USA, 1971 maize, (variety ns)	150G	4.4	1	at planting (21 May)	ns	83[a] 103[a]	< 0.05 < 0.05	idem
Ames, IA,	150G	8.8	1	at planting	ns	83[a]	< 0.05	idem

Location, year, crop, (variety)	Form.	kg ai/ha	No	Method, timing	Soil	PHI, days	Total, mg/kg eq	Reference
USA, 1971 maize, (variety ns)				(21 May)		103[a]	< 0.05	
Benedict, NE, USA, 1981, maize (Pioneer 3541)	150G	1.2	1	banded at cultivation, (9 June, 41 d after planting)	silt loam pH ns 2.8% om % clay ns	84[a]	< 0.05 no recoveries	Higham, 1981 [PA-731-010]

a Green forage. Maize plant harvested before normal harvest time. The reviewer assumes that this is the whole plant with immature grains and therefore the plant is still green.

b Green fodder. Maize plant harvested at the same time as sweet corn cobs. The reviewer assumes that this is the plant without corn cobs. Based on commercial practices, plants are harvested green. Confirmed by manufacturer.

c Samples are assumed to be replicate field samples by the present reviewer, therefore the mean value is calculated.

Table 51. Total phorate-related residues (oxidizable to phoratoxon sulfone) in dry maize plants (fodder) from granular soil treatments at planting.

Location, year, crop (variety)	Form.	kg ai/ha	No	Method, timing	Soil	PHI, days	Total, mg/kg eq	Reference
Clinton, WI, USA, 1971 maize, (variety ns)	150G	2.2	1	at planting (4 April)	ns	116[c]	< 0.05	Peterson, 1973 [PA-730-013]
Clinton, WI, USA, 1971 maize, (variety ns)	150G	4.4	1	at planting (4 April)	ns	116[c]	< 0.05	idem
Ames, IA, USA, 1971 maize, (variety ns)	150G	2.2	1	at planting (21 May)	ns	137[c]	< 0.05	idem
Ames, IA, USA, 1971 maize, (variety ns)	150G	4.4	1	at planting (21 May)	ns	137[c]	< 0.05	idem
Ames, IA, USA, 1971 maize, (variety ns)	150G	8.8	1	at planting (21 May)	ns	137[c]	< 0.05	idem
Benedict, NE, USA, 1981, maize (Pioneer 3541)	150G	1.2	1	banded at cultivation, (9 June, 41 d after planting)	silt loam pH ns 2.8% om % clay ns	119[c]	< 0.05 no recoveries	Higham, 1981 [PA-731-010]
York, NE, USA; 1985 maize (Pioneer 3377)	200G	1.46	2	1st banded at planting (21May) 2nd banded at cultivation at 4-6 leaf stage (10 June)	silt loam pH ns 3.9% om %clay ns	106[c] 121[c]	< 0.05 < 0.05 no recoveries	Higham, 1986 [PA-730-055]
York, NE, USA; 1985 maize (Pioneer 3377)	200G	2.92	2	1st banded at planting (21May) 2nd banded at cultivation at 4-6 leaf stage (10 June)	silt loam pH ns 3.9% om %clay ns	106[c] 121[c]	0.13 < 0.05 no recoveries	idem
York, NE, USA; 1985 maize (Pioneer 3377)	200G	1.46 1.12	2	1st banded at planting (21 May) 2nd broadcast over the top at 2.1 m height (26 Aug)	silt loam pH ns 3.9% om %clay ns	29[c] 44[c]	0.22 0.23 no recoveries	idem
York, NE, USA; 1985 maize (Pioneer 3377)	200G	2.91 2.24	2	1st banded at planting (21 May) 2nd broadcast over the top at 2.1 m height (26 Aug)	silt loam pH ns 3.9% om %clay ns	29[c] 44[c]	0.13 0.97 no recoveries	idem

Location, year, crop (variety)	Form.	kg ai/ha	No	Method, timing	Soil	PHI, days	Total, mg/kg eq	Reference
York, NE, USA; 1985 maize (Pioneer 3377)	200G	1.46 1.12	2	1st banded at cultivation at 4-6 leaf stage (10 June) 2nd broadcast over the top at 2.1 m height (26 Aug)	silt loam pH ns 3.9% om %clay ns	29[c] 44[c]	0.09 0.14 no recoveries	idem
York, NE, USA; 1985 maize (Pioneer 3377)	200G	2.92 2.24	2	1st banded at cultivation at 4-6 leaf stage (10 June) 2nd broadcast over the top at 2.1 m height (26 Aug)	silt loam pH ns 3.9% om %clay ns	29[c] 44[c]	0.46 0.42 no recoveries	idem
York, NE, USA; 1985 maize (McCurdy 3784)	200G	1.46	2	1st banded at planting (4 May) 2nd banded at cultivation at 6-8 leaf stage (10 June)	silt loam pH ns 3.9% om %clay ns	107[c] 122[c]	< 0.05 < 0.05 no recoveries	Higham, 1986 [PA-730-056]
York, NE, USA; 1985 maize (McCurdy 3784)	200G	2.92	2	1st banded at planting (4 May) 2nd banded at cultivation at 6-8 leaf stage (10 June)	silt loam pH ns 3.9% om %clay ns	107[c] 122[c]	< 0.05 < 0.05 no recoveries	idem
York, NE, USA; 1985 maize, (McCurdy 3784)	200G	1.46 1.12	2	1st banded at planting (4 May) 2nd broadcast over the top at 2.1 m height (26 Aug)	silt loam pH ns 3.9% om %clay ns	29[c] 44[c]	0.09 0.13 no recoveries	idem
York, NE, USA; 1985 maize, (McCurdy 3784)	200G	2.91 2.24	2	1st banded at planting (4 May) 2nd broadcast over the top at 2.1 m height (26 Aug)	silt loam pH ns 3.9% om %clay ns	29[c] 44[c]	0.11 0.10 no recoveries	idem
York, NE, USA; 1985 maize, (McCurdy 3784)	200G	1.46 1.12	2	1st banded at cultivation at 6-8 leaf stage (10 June) 2nd broadcast over the top at 2.1 m height (26 Aug)	silt loam pH ns 3.9% om %clay ns	29[c] 44[c]	0.16 0.09 no recoveries	idem
York, NE, USA; 1985 maize, (McCurdy 3784)	200G	2.92 2.24	2	1st banded at cultivation at 6-8 leaf stage (10 June) 2nd broadcast over the top at 2.1 m height (26 Aug)	silt loam pH ns 3.9% om %clay ns	29[c] 44[c]	1.8 2.0 no recoveries	idem
Monticello, IL, USA, 1986 maize (EK 7782)	136G [b]	1.12	1	banded at planting (16 May)	silt clay loam pH ns 4.2% om 28% clay	133[c]	< 0.05	Higham & Fisher, 1988 [PA-730-031]
Monticello, IL, USA, 1986 maize (EK 7782)	143G [b]	1.12	1	banded at planting (16 May)	silt clay loam pH ns 4.2% om 28% clay	133[c]	< 0.05	idem
York NE, USA, 1986 maize (Pioneer 3377)	136G [b]	1.12	1	banded at planting (19 May)	silt loam pH ns 3.7% om 22% clay	136[c]	< 0.05[a]	Higham & Fisher, 1988 [PA-730-032]
York NE, USA, 1986 maize (Pioneer 3377)	143G [b]	1.12	1	banded at planting (19 May)	silt loam pH ns 3.7% om 22% clay	136[c]	< 0.05	idem
York NE, USA, 1986	143G [b]	2.24	1	banded at planting (19 May)	silt loam pH ns	136[c]	< 0.05	idem

Location, year, crop (variety)	Form.	kg ai/ha	No	Method, timing	Soil	PHI, days	Total, mg/kg eq	Reference
maize (Pioneer 3377)					3.7% om 22% clay			
York NE, USA, 1986 maize (Pioneer 3377)	143G[b]	5.60	1	banded at planting (19 May)	silt loam pH ns 3.7% om 22% clay	136[c]	< 0.05	idem

a. Result of duplicate analyses.

b. The 150 G product consists of two active ingredients with a ratio of 10:1 or 20:1 Thimet (phorate): Asana (esfenvalerate). This results in either 136 g phorate per kg product or 143 g phorate per kg product.

c Dry fodder. Maize plant harvested at the same time as grains. The reviewer assumes that this is the plant without grains. Confirmed by manufacturer.

Table 52. Total phorate-related residues (oxidizable to phoratoxon sulfone) re-analysed for individual metabolites in green maize plants (forage/fodder).

Location, year, (variety)	kg ai/ha	no	PHI, days	Compound	Residue mg/kg (c)	Reference
York, NE, USA; 1985 maize (Pioneer 3377) green fodder	1.46 1.12	2	29	Total	0.22	Higham, 1986 [PA-730-055] Roman, 1987 [PA-730-067]
			.	parent	< 0.05	
			.	phorate sulfoxide	0.06	
			.	phorate sulfone	0.12	
			.	phoratoxon	< 0.05	
			.	phoratoxon sulfoxide	< 0.05	
			.	phoratoxon sulfone	< 0.05	
			44	Total	0.23	
			.	parent	< 0.05	
			.	phorate sulfoxide	< 0.05	
			.	phorate sulfone	0.11	
			.	phoratoxon	< 0.05	
			.	phoratoxon sulfoxide	< 0.05	
			.	phoratoxon sulfone	< 0.05	
					no recoveries	
York, NE, USA; 1985 maize (Pioneer 3377) green fodder	2.91 2.24	2	44	Total	0.97	Higham, 1986 [PA-730-055] Roman, 1987 [PA-730-067]
			.	parent	0.16	
			.	phorate sulfoxide	0.24	
			.	phorate sulfone	0.48	
			.	phoratoxon	< 0.05	
			.	phoratoxon sulfoxide	< 0.05	
			.	phoratoxon sulfone	< 0.05	
					no recoveries	
York, NE, USA; 1985 maize (Pioneer 3377) green fodder	2.92 2.24	2	29	Total	0.46	Higham, 1986 [PA-730-055] Roman, 1987 [PA-730-067]
			.	parent	< 0.05	
			.	phorate sulfoxide	0.08	
			.	phorate sulfone	0.24	
			.	phoratoxon	< 0.05	
			.	phoratoxon sulfoxide	< 0.05	
			.	phoratoxon sulfone	< 0.05	
			44	Total	0.42	
			.	parent	< 0.05	
			.	phorate sulfoxide	0.09	
			.	phorate sulfone	0.28	
			.	phoratoxon	< 0.05	
			.	phoratoxon sulfoxide	< 0.05	
			.	phoratoxon sulfone	< 0.05	
					no recoveries	
York, NE, USA; 1985 maize, (McCurdy 3784) green fodder	2.91 2.24	2	29	Total	1.8	Higham, 1986 [PA-730-056] Roman, 1987 [PA-730-067]
			.	parent	0.32	
			.	phorate sulfoxide	0.43	
			.	phorate sulfone	0.70	
			.	phoratoxon	< 0.05	
			.	phoratoxon sulfoxide	< 0.05	
			.	phoratoxon sulfone	< 0.05	
			44	Total	2.0	

Location, year, (variety)	kg ai/ha	no	PHI, days	Compound	Residue mg/kg (c)	Reference
			. . . . . .	parent phorate sulfoxide phorate sulfone phoratoxon phoratoxon sulfoxide phoratoxon sulfone	0.43 0.42 [a] 0.61 [a] < 0.05 [a] < 0.05 [a] < 0.05 no recoveries	
Arlington, WI, USA, 1985, sweet corn (Jubilee) green fodder	2.91	2	57	Total parent phorate sulfoxide phorate sulfone phoratoxon phoratoxon sulfoxide phoratoxon sulfone	0.11 < 0.05 < 0.05 0.05 < 0.05 < 0.05 < 0.05 no recoveries no controls	Higham, 1986 [PA-723-002] Roman, 1987 [PA-730-067]
Sanford, FL, USA, 1985 sweet corn (Jubilee) green fodder	1.46	1	71	Total parent phorate sulfoxide phorate sulfone phoratoxon phoratoxon sulfoxide phoratoxon sulfone	0.15 < 0.05 < 0.05 0.08 < 0.05 < 0.05 < 0.05 no recoveries no controls	Higham, 1986 [PA-723-003] Roman, 1987 [PA-730-067]
Sanford, FL, USA, 1985 sweet corn (Jubilee) green fodder	2.91	2	37	Total parent phorate sulfoxide phorate sulfone phoratoxon phoratoxon sulfoxide phoratoxon sulfone	0.93, 1.6; mean 1.3 [b] < 0.05 (2); mean < 0.05 [b] 0.14, 0.17; mean 0.16 [b] < 0.05 (2); mean < 0.05 [b] < 0.05, 0.36; mean 0.20 [b] < 0.05, 0.07; mean 0.06 [b] 0.14; 0.20; mean 0.17 [b] no recoveries	Higham, 1986 [PA-723-004] Roman, 1987 [PA-730-067]
Corvallis, OR, USA, 1985 sweet corn (Jubilee) green forage	2.91	2	29	Total parent phorate sulfoxide phorate sulfone phoratoxon phoratoxon sulfoxide phoratoxon sulfone	0.35 < 0.05 0.09 0.18 < 0.05 < 0.05 < 0.05 no recoveries	Higham, 1986 [PA-723-007] Roman, 1987 [PA-730-067]
Corvallis, OR, USA, 1985 sweet corn (Jubilee) green forage	7.29	2	29 . . . . . . 59	Total parent phorate sulfoxide phorate sulfone phoratoxon phoratoxon sulfoxide phoratoxon sulfone Total parent phorate sulfoxide phorate sulfone phoratoxon phoratoxon sulfoxide phoratoxon sulfone	0.98 < 0.05 [a] 0.30 [a] 0.42 [a] < 0.05 < 0.05 < 0.05 0.29 < 0.05 [a] < 0.05 [a] 0.18 < 0.05 [a] < 0.05 [a] 0.06 [a] no recoveries	Higham, 1986 [PA-723-007] Roman, 1987 [PA-730-067]

a Average of duplicate analyses.

b. Samples are assumed to be replicate field samples by the present reviewer, therefore the mean value is calculated.

c. It is not clear from the study reports if the concentrations are expressed as mg/kg eq or as mg/kg for each individual metabolite

Table 53. Total phorate-related residues (oxidizable to phoratoxon sulfone) in green sorghum forage from granular soil treatments at planting or at cultivation.

Location, year (variety)	Form.	kg ai/ha	No	Method, timing	Soil	PHI, d	Total mg/kg eq	Reference
Waco, NE, USA, 1981, (Cargill 50)	150G	1.22	1	banded at cultivation, (16 June, 19 d after planting)	silt loam pH 6.6 4.0% om 12% clay	78[b]	< 0.05 no recoveries	Bohn, 1982 [PA-730-063]
Wilbur, NE, USA, 1981, (GH H500B)	150G	1.22-1.46[a]	1	banded at cultivation, (17 July, 56 d after planting)	silt loam pH 6.0 3.4% om 12% clay	47[b]	0.13 no recoveries	Bohn, 1982 [PA-730-064]
Dorchester, NE, USA, 1981, (Mc Curdy 91)	200G	1.46	1	banded at cultivation, 56 cm height (17 July, 56 d after planting)	silt loam pH 5.9 2.3% om 21 clay	47[b]	< 0.05 no recoveries	Bohn, 1982 [PA-730-065]

a. row spacing not stated, a row spacing of 30-36 inch (76-91 cm) was assumed by the present reviewer as in the other NE, 1981 trials.

b Green forage. Sorghum plant harvested before normal harvest time. The reviewer assumes that this is the whole plant with immature grains and therefore the plant is assumed to be green. Confirmed by manufacturer.

Table 54. Total phorate-related residues (oxidizable to phoratoxon sulfone) in dry sorghum fodder from granular soil treatments at planting or at cultivation.

Location, year (variety)	Form.	kg ai/ha	No	Method, timing	Soil	PHI, days	Total mg/kg eq	Reference
Burlington, CO, USA, 1981, (Pioneer 8451)	150G	1.46	1	banded at cultivation, (6 July, 32 d after planting)	silt loam, pH 7.4 1.8% om 20% clay	95[b]	< 0.05 no recoveries	Roman, 1982 [PA-731-006]
Waco, NE, USA, 1981, (Cargill 50)	150G	1.22	1	banded at cultivation, (16 June, 19 d after planting)	silt loam pH 6.6 4.0% om 12% clay	108[b]	< 0.05 no recoveries	Bohn, 1982 [PA-730-063]
Wilbur, NE, USA, 1981, (GH H500B)	150G	1.22-1.46[a]	1	banded at cultivation, (17 July, 56 d after planting)	silt loam pH 6.0 3.4% om 12% clay	76[b]	< 0.05 no recoveries	Bohn, 1982 [PA-730-064]
Dorchester, NE, USA, 1981, (Mc Curdy 91)	200G	1.46	1	banded at cultivation, 56 cm height (17 July, 56 d after planting)	silt loam pH 5.9 2.3% om 21 clay	76[b]	< 0.05 no recoveries	Bohn, 1982 [PA-730-065]
Dalhart, TX, USA, 1985, (Pioneer)	200G	1.46 1.12	2	1st banded at planting (27 May) 2nd by air, foliar (24 August)	sandy loam pH 7.3 0.5-1.0% om %clay ns	30[b] 45[b]	< 0.05 < 0.05	Higham, 1987 [PA-730-035]
Dalhart, TX, USA, 1985, (Pioneer)	200G	2.91 2.24	2	1st banded at planting (27 May) 2nd by air, foliar (24 August)	sandy loam pH 7.3 0.5-1.0% om %clay ns	30[b] 45[b]	< 0.05 < 0.05	idem
Mt. Hope, KS, USA, 1985, (Dekalb DK 424)	200G	1.46 1.12	2	1st banded at planting (17 June) 2nd broadcast, foliar (18 August)	silt loam details ns	30[b] 46[b]	< 0.05 < 0.05[b]	Higham, 1987 [PA-730-036]
Mt. Hope, KS, USA, 1985, (Dekalb DK 424)	200G	2.91 2.24	2	1st banded at planting (17 June) 2nd broadcast, foliar (18 August)	silt loam details ns	30[b] 46[b]	< 0.05 0.06	idem
Mt. Hope, KS, USA, 1985, (Dekalb DK 424)	200G	1.46 1.12	2	1st banded at planting (17 June) 2nd by air, foliar (18 August)	silt loam details ns	30[b] 46[b]	< 0.05[c] < 0.05	Higham, 1987 [PA-730-037]
Mt. Hope,	200G	2.91	2	1st banded at planting	silt loam	30[b]	< 0.05	idem

Location, year (variety)	Form.	kg ai/ha	No	Method, timing	Soil	PHI, days	Total mg/kg eq	Reference
KS, USA, 1985, (Dekalb DK 424)		2.24		(17 June) 2nd by air, foliar (18 August)	details ns	46[b]	< 0.05	
Plainview, TX, USA, 1985, (PAG 4462)	200G	1.46 1.12	2	1st banded at planting (27 May) 2nd broadcast, foliar (7 Sept)	sandy clay loam pH ns 1.0-1.5% om % clay ns	30[b] 44[b]	< 0.2 [c] < 0.2 [c]	Higham, 1987 [PA-730-038]
Plainview, TX, USA, 1985, (PAG 4462)	200G	2.91 2.24	2	1st banded at planting (27 May) 2nd broadcast, foliar (7 Sept)	sandy clay loam pH ns 1.0-1.5% om % clay ns	30[b] 44[b]	< 0.2 [c] < 0.2 [c]	idem

a. row spacing not stated, a row spacing of 30-36 inch (76-91 cm) was assumed by the present reviewer as in the other NE, 1981 trials.

b Dry fodder. Sorghum plant harvested at the same time as sorghum grains. The reviewer assumes that this is the dry plant without grains. Confirmed by manufacturer.

c Average of two analyses

Miscellaneous fodder and forage crops

For description of trials, see primary crop.

Table 55. Total phorate-related residues (oxidizable to phoratoxon sulfone) in cotton dry fodder[a] from granular soil treatments at planting or at cultivation.

Location, year (variety)	Form.	kg ai/ha	No	Method, timing	Soil	PHI, days	Total, mg/kg eq	Reference
Glen Allen, MS, USA, 1985 (DPL 41)	200 G	1.79 2.47	2	1st in furrow, at planting 7 May 2nd side-dressed 10 July	silt loam, pH 6.8 1.0% om %clay ns	65	< 0.05	Higham, 1987 [PA-750-005]
Glen Allen, MS, USA, 1985 (DPL 41)	200 G	3.59 4.93	2	1st in furrow, at planting 7 May 2nd side-dressed 10 July	silt loam, pH 6.8 1.0% om %clay ns	65	0.22	idem
Plainview, TX, USA 1985 (Paymaster)	200 G	1.79 2.47	2	1st in furrow, at planting 31 May 2nd side-dressed 14 Sept	clay loam pH 7.5 1.5% om %clay ns	64	0.16	Higham, 1987 [PA-750-006]
Plainview, TX, USA 1985 (Paymaster)	200 G	3.59 4.93	2	1st in furrow, at planting 31 May 2nd side-dressed 14 Sept	clay loam pH 7.5 1.5% om %clay ns	64	0.50[b]	idem
Belle Mina, AL, USA 1985 (DPL 50)	200 G	0.84	1	in furrow, at planting 19 April	ns	137	< 0.05	Higham, 1987 [PA-750-008]
Belle Mina, AL, USA 1985 (DPL 50)	200 G	1.79 2.47	2	1st in furrow, at planting 19 April 2nd side-dressed 5 June	ns	90	< 0.05	idem
Belle Mina, AL, USA 1985 (DPL 50)	200 G	3.59 4.93	2	1st in furrow, at planting 19 April 2nd side-dressed 5 June	ns	90	< 0.05	idem

Location, year (variety)	Form.	kg ai/ha	No	Method, timing	Soil	PHI, days	Total, mg/kg eq	Reference
Dysart, AZ, USA 1985 (DPL 90)	200 G	1.79 3.59	2	1st in furrow, at planting 1 May 2nd side-dressed 27 August	ns	61	1.7[b]	Higham, 1987 [PA-750-009]
Dysart, AZ, USA 1985 (DPL 90)	200 G	2.47 4.93	2	1st in furrow, at planting 1 May 2nd side-dressed 27 August	ns	61	3.2	idem

a Dry fodder. Cotton plant harvested at the same time as cotton seeds. The reviewer assumes that this is the plant without seeds. Based on commercial practices then, plants are harvested dry. Confirmed by manufacturer.

b Average of two analyses.

Table 56. Total phorate-related residues (oxidizable to phoratoxon sulfone) in sugarbeet tops from granular soil treatments at planting or post-emergence.

Location, year (variety)	Form.	kg ai/ha	No	Method, timing	Soil	PHI, days	Total mg/kg eq	Reference
Northwood, ND, USA 1985 (Bush Johnson 19)	200G	1.68	1	by air, post-emergence foliar, (21 Aug: 85 d after planting)	silt loam pH ns 3.0-3.2% om % clay ns	1 3 7 14 21 30	0.72 0.69 0.24 0.19[a] < 0.08 < 0.08	Higham, 1987 [PA-724-020]
Northwood, ND, USA 1985 (Bush Johnson 19)	200G	3.36	1	by air, post-emergence foliar, (21 Aug: 85 d after planting)	silt loam pH ns 3.0-3.2% om % clay ns	1 3 7 14 21 30	0.69 1.9 0.98 1.4 0.45 0.16	idem
Northwood, ND, USA 1985 (Bush Johnson 19)	200G	1.68	2	1st in a band at planting (3 May); 2nd broadcast post-emergence (22 Aug)	silt loam pH ns 3.0-3.2% om % clay ns	21 30	0.36[a] 0.44	Higham, 1987 [PA-724-021]
Northwood, ND, USA 1985 (Bush Johnson 19)	200G	3.36	2	1st in a band at planting (3 May); 2nd broadcast post-emergence (22 Aug)	silt loam pH ns 3.0-3.2% om % clay ns	21 30	1.2 0.22	idem
Northwood, ND, USA 1985 (Bush Johnson 19)	200G	1.68	2	1st in furrow at planting (3 May); 2nd broadcast post-emergence (22 Aug)	silt loam pH ns 3.0-3.2% om % clay ns	21 30	0.57 1.1	idem
Northwood, ND, USA 1985 (Bush Johnson 19)	200G	3.36	2	1st in furrow at planting (3 May); 2nd broadcast post-emergence (22 Aug)	silt loam pH ns 3.0-3.2% om % clay ns	21 30	1.4 1.0	idem
Kimberly, ID, USA 1985 (WS 88)	200G	1.68	1	drilled to the side of the seed at planting (24 April)	silt loam pH 8.0 1.0% om % clay ns	149	< 0.05 (no recoveries)	Peterson, 1987 [PA-724-024]
Kimberly, ID, USA 1985 (WS 88)	200G	3.36	1	drilled to the side of the seed at planting (24 April)	silt loam pH 8.0 1.0% om % clay ns	149	< 0.05 (no recoveries)	idem
Kimberly, ID, USA 1985 (WS 88)	200G	1.68	1	banded over the row at planting (24 April)	silt loam pH 8.0 1.0% om % clay ns	149	< 0.05 (no recoveries)	idem

Location, year (variety)	Form.	kg ai/ha	No	Method, timing	Soil	PHI, days	Total mg/kg eq	Reference
Kimberly, ID, USA 1985 (WS 88)	200G	3.36	1	banded over the row at planting (24 April)	silt loam pH 8.0 1.0% om % clay ns	149	< 0.05 (no recoveries)	idem
Kimberly, ID, USA 1985 (WS 88)	200G	1.68	1	banded post emergence on foliage (11 June: 48 d after planting)	silt loam pH 8.0 1.0% om % clay ns	101	< 0.05 (no recoveries)	idem
Kimberly, ID, USA 1985 (WS 88)	200G	3.36	1	banded post emergence on foliage (11 June: 48 d after planting)	silt loam pH 8.0 1.0% om % clay ns	101	< 0.05 (no recoveries)	idem
Mendota, CA, USA 1985 (SSE2)	200G	1.68	2	1st in a band at planting (6 Mar); 2nd broadcast post-emergence; (22 May)	clay loam pH 8.2 1.0% om %clay ns	0 3 7 14 21 28	0.44 0.82 1.2 1.5 < 0.3 < 0.3	Higham, 1987 [PA-724-025]
Mendota, CA, USA 1985 (SSE2)	200G	3.36	2	1st in a band at planting (6 Mar); 2nd broadcast post-emergence; (22 May)	clay loam pH 8.2 1.0% om %clay ns	0 3 7 14 21 28	0.90 0.67 0.19 0.65[a] < 0.3 < 0.3[a]	idem
Mendota, CA, USA 1985 (SSE2)	200G	1.68	1	by air, foliar post-emergence (22 May, 77 d after planting)	clay loam pH 8.2 1.0% om %clay ns	0 3 7 14 21 28	< 1.4 < 1.4 < 1.4[a] < 1.4 < 1.4 < 1.4	Higham, 1987 [PA-724-026]
Mendota, CA, USA 1985 (SSE2)	200G	3.36	1	by air, foliar post-emergence (22 May, 77 d after planting)	clay loam pH 8.2 1.0% om %clay ns	0 3 7 14 21 28	< 1.4 < 1.4 < 1.4 < 1.4 < 1.4[a] < 1.4	idem

a Average from duplicate analysis

FATE OF RESIDUES IN STORAGE AND PROCESSING

In storage

Phorate is not registered for use in stored products. The Meeting received information on the fate of residues during storage of potatoes at ambient temperatures.

One study was undertaken to investigate the decline in residues for field treated potatoes stored at ambient temperatures (Leonard, 1992: PA-724-008). To ensure presence of residues at harvest, potato plants were treated at planting with a granulate formulation of phorate at an exaggerated rate of 16.7 kg ai/ha. Replicate samples of potato tubers (2.3 kg each) were taken 125 DAT and were stored for 23 d at 21 °C. Total phorate-related residues (oxidizable to phoratoxon sulfone) were determined by GC-FPD, following method M-1705. The reported LOQ is 0.05 mg/kg eq for all commodities.

Table 57 presents the results of the study. Results were not corrected for concurrent method recovery (84%-94%), or for matrix interferences (< 0.3 LOQ). Results show high variability within replicate field samples and residues decline rapidly after 9 d of storage at ambient temperatures.

Table 57. Residue decline of field treated potatoes after storage at ambient temperatures (21 °C).

Location, year, (variety)	Treatment	Storage (d)	Total residues (mg/kg eq) mean	range	RSD_r	n	% remaining	
Northwood, ND; USA, 1991, (Northchip)	200 G 1x 16.7 kg ai/ha PHI 125 d	0 9 23	0.69[a] 0.69[a] 0.23[a]	0.06 - 1.8 0.15 - 1.4 < 0.05 - 0.43	91% 88% 74%	10 5 4	100% 100% 33%	Leonard, 1992, [PA-724-008]

a Average result of n replicate field samples (2.3 kg each)

In processing

The Meeting received information on the fate of incurred residues of phorate during the processing of potatoes, maize and coffee beans.

Processing studies on potatoes tubers

Study 1. A processing study was undertaken in which field treated potatoes were processed into flakes, chips, and granules (Shimel, 1987: PA-724-022). A granulate formulation of phorate was applied in-furrow at planting at rates equivalent to 3.91 or 7.96 kg ai/ha. Potato tubers were collected at 138 d post-treatment. Samples for processing were placed into cold storage (temperature not stated) for 92-99 d. Tubers were processed into chips, flakes and granules according to commercial processing on a laboratory scale.

Chips processing: Potato tubers (4.5 kg) were subsequently washed, peeled, washed, trimmed, and sliced. Slices were washed at 48-54 °C to remove starch, fried at 185 °C in vegetable oil for 60-70 sec and deoiled & salted (= chips). Potato chips contain on average 2-3% water and 30-35% oil. Mass fractions (mass of processed product relative to mass of RAC) were 4.5% for peels plus trimmings (raw livestock feed), 95.5% for unwashed slices, and 28.6% for chips.

Flake processing: Potato tubers (15 kg) were subsequently washed, steam peeled for 75 sec at 100 psi, scrubbed to remove peels, trimmed, and sliced into 1.3-1.6 cm thick slices. Slices were spray washed at 48-54 °C to remove starch, pre-cooked at 71-74 °C for 20 minutes, cooled to 27-32 °C for 20 min, steam cooked at 94-100 °C for 35-45 min. The cooked slices were mashed, mixed with food additives and dried into a thin sheet in a drum drier at 162-170 °C (20 sec/rev; 80-100 psi steam) until a moisture content of 7.0-7.5% was reached. Thereafter flakes were milled to size (= flakes). Mass fractions (mass of processed product relative to mass of RAC) were 8.0% for peels plus trimmings (raw livestock feed), 95.5% for unwashed slices, and 13.3%-14.3% = 13.8% for flakes.

Granule processing: Potato tubers (12-18 kg) were treated as for flake processing up to mixing with food additives. Thereafter the potato mash was subdivided into 1 kg subsamples (A-H and G), which were stored frozen for 43-71 d. Subsamples A was thawed, dried to 10% water on a fluid bed dryer at 54 °C. Sub-sample B was thawed, added, conditioned for 30 min and the drying process was repeated until 10% water content. In the same way thawed subsamples C-H were added and dried. The dried sample was mixed with thawed sub-sample G at 52 °C for 15 min, conditioned at 38-43 °C for 30 min and dried to 8-10% moisture on a fluid bed dryer at 71 °C. Potato mash was treated with a scalping sifter on a 30 mesh screen. The < 30 mesh material was cooled to 38 °C until 7.0-7.5% moisture content and was sifted on a 60 mesh screen (= potato granules). Material remaining on the 30 mesh and 60 mesh screens was mixed and was used as processed livestock feed. Mass fractions (mass of processed product relative to mass of RAC) were 8.0% for peels plus trimmings (raw livestock feed), 95.5% for unwashed slices, 15.4% for material remaining on 30 and 60 mesh screens (processed livestock feed), and 15.4% for granules.

Samples were stored at -23 °C or lower. Although storage times were not stated, the maximum storage time is 236 d. The storage period for RAC samples is covered by the 2.5 year storage stability study on potatoes. Storage stability studies on processed potato commodities have not been submitted and therefore accuracy of the residue data is unknown. Total phorate-related residues (oxidizable to phoratoxon sulfone) were determined by GC-FPD. Potato tubers were analysed according to method M-1620 while potato chips, flakes and granules were analysed following method M-1705. The reported LOQ is 0.05 mg/kg eq for both methods and for all commodities. Because of matrix interferences in method validation, the valid LOQ was increased to 0.06 mg/kg eq for potato flakes and 0.09 mg/kg eq for potato granules.

The results are summarised in Table 58. Results were not corrected for concurrent method recoveries (86% RAC, 116% potato granules), nor for matrix interferences (< 0.3 LOQ). Because both treatments resulted in non-quantifiable residues in potato tubers, processing factors or transference factors could not be calculated.

Study 2. A processing study was undertaken in which field treated potatoes were processed into flakes, chips, and granules (Devine and Green, 1990: PA-724-014). A granular formulation of phorate was applied in-furrow at planting followed by post-emergence band treatment 17 d later, at rates equivalent to 7.96 and 3.91 kg ai/ha. Samples were collected earlier than normal to ensure residues were found at 64 DAT. Samples for processing were placed for 40 hrs at ambient temperatures, for 9 d at cold storage (-1 °C) and for 15 d at cool storage (10-21 °C). Tubers were processed into chips (18 kg), flakes (48-54 kg) and granules (48-54 kg) according to commercial processing procedures but on a laboratory scale, as described for study 1. Mass fractions are shown in Table 58.

Samples were stored frozen for 4 to 6 months (temperature not stated). The storage period for RAC samples is covered by the 2.5 year storage stability study on potatoes. Storage stability studies on processed potato commodities have not been submitted and therefore accuracy of residue data is unknown. Total phorate-related residues (oxidizable to phoratoxon sulfone) were determined by GC-FPD. Potato tubers were analysed according to Method M-1620 while potato chips, flakes and granules were analysed following Method M-1705. The reported LOQ is 0.05 mg/kg eq for both methods and for all commodities. Because of matrix interferences in method validation, the valid LOQ was increased to 0.06 mg/kg eq for potato flakes and 0.09 mg/kg eq for potato granules.

The results are summarised in Table 58. Residue mass balance could not be verified, because waste processing fractions have not been analysed. Recoveries were not verified and therefore performance of the method at the time of sample analysis is unknown. Because of matrix interferences, the LOQ was increased to 0.032/0.3=0.1 mg/kg eq for potatoes (RAC) and to 0.016/0.3 = 0.06 mg/kg eq for chips. For one trial, this resulted in non-quantifiable residues for the potato tubers (RAC), and therefore no processing factors or transference factors could be calculated for this trial.

Study 3. A processing study was undertaken in which field treated potatoes were cooked, baked or fried (Leonard, 1991: PA-724-013). To ensure presence of residues at harvest, potato plants were treated at planting with a granulate formulation of phorate at an exaggerated rate of 16.6 kg ai/ha. Samples of potato tubers (45 kg) were taken 95 DAT. Samples for processing were stored for 9-18 d subsequently at cool conditions, ambient conditions and refrigerated conditions (temperatures not stated). Tubers were divided into subfractions which underwent various processing treatments according to household practices.

Washed: Potatoes (2.3 kg) were washed with water at twice the weight of the potatoes

Peeled: Potatoes (3.2-3.6 kg) were washed (see above) and peeled. Both peeled potatoes and raw peels were analysed.

Baked with peels: Potatoes (2.3 kg) were washed (see above) and punctured (twice). Potatoes were placed in a preheated oven at 218 C for 50-70 min, until peels are crisp.

Baked without peels: Potatoes (4.5-6.8 kg) were baked as above. The peels were removed from the baked potatoes. Both baked potatoes and baked peels were analysed.

Boiled with peels: Potatoes (2.3-2.7 kg) were size selected at less than 7.6 cm diameter. The potatoes were washed (see above) and were placed in sufficient saucepans with 1.25 L distilled, deionized water each in such a way that potatoes are completely covered with water. The water is brought to boiling and thereafter the potatoes are boiled for 35 min. Potatoes are cooled to room temperature.

Boiled without peels: Potatoes (5.4 kg) were boiled as above. Potatoes were then peeled. Both peel and flesh from boiled potatoes were then analysed.

French fries: Potatoes (4.5-5.4 kg) were washed (see above) and peeled. Potatoes were sliced into 64 mm segments and allowed to dry. The potatoes are fried in preheated cooking oil at 190 °C for 5-6 minutes until golden brown. Fries are then placed on a towel to absorb excess oil.

Samples were stored at -10 °C or lower for a maximum of 3 months. The storage period for RAC samples is covered by the 2.5 year storage stability study on potatoes. Storage stability studies on processed potato commodities have not been submitted and therefore accuracy of residue data is unknown. Total phorate-related residues (oxidizable to phoratoxon sulfone) were determined by GC-FPD, as described in method M-1705. The reported LOQ is 0.05 mg/kg eq for all commodities. A method validation report on raw potatoes (+/- peel), raw peels, cooked potatoes (+/- peels), cooked peels, baked potatoes (+/- peel), baked peels, dry peels, french fries, wash or cooking water is not available and accuracy of residue concentrations is therefore unknown.

Table 58 presents the results of the study. Results were not corrected for concurrent method recovery (78%-106%), or for matrix interferences (< 0.3 LOQ). Mass fractions were not determined and therefore transference could not be calculated.

Study 4. A processing study was undertaken in which field treated potatoes were cooked, baked or fried (Leonard, 1992: PA-724-009). To ensure presence of residues at harvest, potato plants were treated at planting with a granulate formulation of phorate at an exaggerated rate of 17.6 kg ai/ha. Samples of potato tubers were taken 126 DAT (82 kg control, 320 kg treated). Samples for processing were stored for 1 day at ambient conditions (21 °C). Tubers were divided into subfractions which underwent various processing treatments according to household practices. Mass fractions are shown in Table 58.

Washing: Potatoes (23 kg) were washed with water at twice the weight of the potatoes. Both potatoes and washing water were analysed.

Peeling: Potatoes (23 kg) were washed (see above) and peeled. Both peeled potatoes and raw peels were analysed.

Boiling: Potatoes (23 kg) were washed (see above) and were split in two portions. One portion was peeled, while the other portion was not. Unpeeled potatoes, peeled potatoes and peels were boiled at unspecified conditions. Boiled unpeeled potatoes, boiled peeled potatoes, boiled peels and boiling water were analysed.

Baking: Potatoes (23 kg) were washed (see above) and were split in two portions. One portion was peeled, while the other portion was not. Peeled potatoes, unpeeled potatoes and peels were baked at unspecified conditions. Baked unpeeled potatoes, baked peeled potatoes and baked peels were analysed

French fries: Potatoes (23 kg) were washed (see above). Half the portion was taken for further processing and was peeled. Potatoes were fried at unspecified conditions. Both French fries and the oil were analysed.

Samples of raw and processed potatoes, washing water, boiling water and frying oil were kept frozen at -10°C for a maximum of 10 months. The storage period for RAC samples is covered by the

2.5 year storage stability study on potatoes. Storage stability studies on processed potato commodities have not been submitted and therefore accuracy of residue data is unknown. Total phorate-related residues (oxidizable to phoratoxon sulfone) were determined by GC-FPD, following method M-1705. The reported LOQ is 0.05 mg/kg eq for all commodities. A method validation report on raw potatoes (+/- peel), raw peels, cooked potatoes (+/- peels), cooked peels, baked potatoes (+/- peel), baked peels, dry peels, french fries, wash or cooking water is not available and accuracy of residue concentrations is therefore unknown.

Table 58 presents the results of the study. Results were not corrected for concurrent method recovery (78% - 119% for RAC, 65%-101% for wash water), nor for matrix interferences (< 0.3 LOQ for all commodities). Concurrent method recoveries for processed commodities were not verified. Because of matrix interferences, the LOQ for baked peels was increased to 0.016/0.3 = 0.06 mg/kg eq. Residue mass balances could be verified for all processing procedures.

- For washing; 32% of original residues were found in washed potatoes and only 2.7% of residue was found in the washing water, i.e. 66% of original residues is not accounted for.

- For peeling; of the 32% of original residues found in washed potatoes, 21% of original residue were found in washed, peeled potatoes while 11% of original residues was found in washed peels. No residues are lost during peeling.

- For boiling with peel; of the 32% of original residue found in washed potatoes, 14% of original residue were found in boiled unpeeled potatoes, while only 3.4% of original residues was found in the boiling water, i.e. 15% of original residues is not accounted for.

- For boiling without peel; of the 29% of original residues found in washed potatoes, 9.3% of original residue remained in peeled, cooked potatoes and 2.9% of original residues remained in the cooked peel, while only 3.4% of original residue was found in the water, i.e. 14% of residues are not accounted for.

- For baking with peel; of the 32% of original residues found in washed potatoes, 22% of original residue remained in unpeeled baked potatoes, i.e. 10% of original residues are not accounted for.

- For baking without peel; of the 32% of original residues found in washed potatoes, 17% of original residue remained in peeled baked potatoes and 8.8% of original residue remained in baked peel, i.e. 6.1% of original residue is not accounted for.

- For French frying; of the 21% of original residues found in washed peeled potatoes, 17% of original residue was found in the French fries and 2.2% of original residue was found in the oil, i.e. 1.2% of original residue is not accounted for.

Results from residue mass balance show, that during washing, cooking, baking or frying a large part of the residues is lost (66%−81% of original residues). It is possible that these residues have degraded to compounds not measured by the analytical method. The nature and location of these degradation products is unknown.

Study 5. A processing study was undertaken in which field treated potatoes were microwave cooked or were processed into chips and granules (Leonard, 1992: PA-724-008). To ensure presence of residues at harvest, potato plants were treated at planting with a granulate formulation of phorate at an exaggerated rate of 16.7 kg ai/ha. Samples of potato tubers were taken 125 DAT (270 kg). Samples for processing were stored for 6 d at ambient temperatures (21°C). Tubers were divided into subfractions which underwent various processing treatments, according to household practices (microwave cooking) or commercial processing on a laboratory scale (chips, granules). Mass fractions are shown in table 58.

Washing and peeling: Potatoes (227 kg) were washed in batches of 45 kg with water at twice the weight of the potatoes. A subfraction of the washed potatoes (170 kg) was peeled. A subfraction of the peels (23 kg) was dried. Raw potatoes, washed potatoes, washing water, peeled potatoes, raw peels, and dry peels were analysed.

Granule processing: Potatoes (14 kg) were washed with water at twice the weight of the potatoes. A subfraction of the washed potatoes (12 kg) was peeled and rinsed with water. Subsequently the potatoes were divided in two portions. The first portion underwent a process of dicing, cooking, washing, drying, grinding, and formation of seed granules. The second portion underwent a process of dicing, cooking and washing. Both portions were blended, tempered, dried, ground and formed into granules. A detailed description of the process is not available. Granules were analysed.

Chips processing: Potatoes (14 kg) were washed with water at twice the weight of the potatoes. A subfraction of the washed potatoes (12 kg) was peeled and rinsed with water. Potatoes were sliced, blanched in water at 88 °C and fried in oil to obtain potato chips. A detailed description of the process is not available. Chips and oil were analysed.

Microwave cooking: Potatoes (21 kg) were washed with water at twice the weight of the potatoes. A subfraction of the washed potatoes (10 kg) were microwaved. The skin of the potatoes was pricked before microwaving. Potatoes were microwaved in 15 batches of 4 potatoes each at the maximum temperature until completely cooked (6-8 min for 4 potatoes of 170-220 g each). A detailed description of the process is not available. Cooked potatoes were analysed.

Samples of raw and processed potatoes were kept frozen at -10 °C for a maximum of 5 months. The storage period for RAC samples is covered by the 2.5 year storage stability study on potatoes. Storage stability studies on processed potato commodities have not been submitted and therefore accuracy of residue data is unknown. Total phorate-related residues (oxidizable to phoratoxon sulfone) were determined by GC-FPD, following method M-1705. The reported LOQ is 0.05 mg/kg eq for all commodities. Because of matrix interferences in method validation, the valid LOQ was increased to 0.09 mg/kg eq for potato granules. A method validation report on raw potatoes (+/- peel), wet/dry peels, cooked potatoes is not available and accuracy of residue concentrations is therefore unknown.

Table 58 presents the results of the study. Results were not corrected for concurrent method recovery (72%-122% for all commodities), nor for matrix interferences (< 0.3 LOQ for all commodities). Residue mass balances could be verified for all processing procedures. All samples were analysed on an as received basis.

- For washing, 49% of original residues were found in washed potatoes and only 1.1% of original residues were found in the washing water, i.e. 50% of original residues are not accounted for.

- For peeling, of the 49% of original residues found in washed potatoes, 24% of original residues were found in washed, peeled potatoes while 14% of original residues was found in washed peels, i.e. 11% of original residues is not accounted for. Upon drying, 6.5% of original residues remained in the dry peels i.e. 7.4% of original residues are not accounted for.

- For microwave boiling with peels, of the 49% of original residues found in washed potatoes, 29% of original residues were found in microwave boiled unpeeled potatoes, i.e. 21% of original residues is not accounted for.

- For granule processing, of the 24% of original residues found in washed peeled potatoes, 21% of original residues remained in granules, i.e. 2.4% of original residues is not accounted for.

- For chips processing, of the 24% of original residues found in washed peeled potatoes, 2.1% of original residues remained in chips and 0.3% of original residues were found in the oil, i.e. 21% of original residues are not accounted for.

Table 58. Total phorate-related residues (oxidizable to phoratoxon sulfone) in processed commodities of field treated potatoes.

Location, year, (variety)	Form, kg ai/ha	DAT	Commodity	Total mg/kg eq	%M	P-factor	%T	Reference
Jerome, ID, USA, 1986 (Russet Burbank)	200 G 1x 3.92	138	RAC chips flakes granules	< 0.05 < 0.05 < 0.06 < 0.09	- 12.8% 13.8% 15.4%	-	-	Shimel, 1987 [PA-724-022]
Jerome, ID, USA, 1986 (Russet Burbank)	200 G 1x 7.96	138	RAC chips flakes granules	< 0.05 < 0.05 < 0.06 < 0.09	- 12.8% 13.8% 15.4%	-	-	Shimel, 1987 [PA-724-022]
Jerome, ID, USA, 1987 (Russet Burbank)	200 G 1x 7.96 1x 3.92	64[b]	RAC chips flakes granules	< 0.1[a] < 0.06 0.19 0.33 no recoveries	- 9.3% 4.5% 1.5%	-	-	Devine and Green, 1990 [PA-724-014]
Jerome, ID, USA, 1987 (Russet Burbank)	200 G 1x 7.96 1x 3.92	64[b]	RAC chips flakes granules	0.20[a] < 0.06 0.31 0.73 no recoveries	- 8.8% 4.5% 1.5%	- < 0.30 1.6 3.6	- < 2.6% 7.2% 5.4%	Devine and Green, 1990 [PA-724-014]
Northwood, ND; USA, 1990, (Norchip)	200 G 1x 16.6	95	RAC washed peeled boiled with peels boiled without peels boiled peels baked with peels baked without peels baked peels French fries	0.56[a] 0.72 1.0 0.36 0.61 0.40 0.24 0.20 0.24 0.63[a]	-	- 1.3 1.8 0.64 1.1 0.71 0.43 0.36 0.43 1.1	-	Leonard, 1991, [PA-724-013]
Jerome, ID; USA, 1991, (Russet Burbank)	200 G 1x 17.6	126	RAC washed peeled raw peels raw peels raw peels boiled with peel boiled without peel boiled peels baked with peel baked without peel baked peels French fries	1.3 0.41 0.32 0.95[a] 0.68 0.82 0.17 0.14 0.18[a] 0.37 0.35[a] 3.1 0.49	- 100% 85% 15% 17% 17% 104% 86% 21% 77% 62% 3.7% 46%	- 0.32 0.25 0.73 0.52 0.63 0.13 0.11 0.14 0.28 0.27 2.4 0.38	- 32% 21% 11% 8.7% 11% 14% 9.3% 2.9% 22% 17% 8.8% 17%	Leonard, 1992 [PA-724-009]
Northwood, ND; USA, 1991, (Norchip)	200 G 1x 16.7	125	RAC washed peeled raw peels dry peels granules chips microwaved with peel	0.69 0.34 0.19 0.60 1.5 0.85 < 0.05 0.25	- 100% 86% 16% 3% 17% 29% 79%	- 0.49 0.28 0.87 2.2 1.2 < 0.07 0.36	- 49% 24% 14% 6.5% 21% < 2.1% 29%	Leonard, 1992 [PA-724-008]

%M (mass fraction) is mass of processed product (corrected for subfractionation): mass of starting material (RAC) x 100%

P-factor (processing factor) is residue in processed commodity: residue in RAC

%T (percentage transference of residue) is p-factor x mass fraction

a Average of two replicate analyses

b Sample obtained at earlier than normal harvest time

Processing studies on maize

Processing studies were undertaken in which field treated maize was processed into flour and oil (Potts, 1986: PA-730-042 and Potts, 1987: PA-730-041, PA-730-039, and PA-730-034). Maize plots were treated three times with a granulate phorate formulation at rates of applications between 2.2 and 7.9 kg ai/ha. Samples of maize grain were harvested 30 DAT. Samples were kept frozen at -1 °C until processing (time period not stated). The grain was milled and processed into oil on a small-scale.

Milling and sieving: Foreign and maize plant materials are removed by aspiration and/or screening. Moisture of the kernel was adjusted to 22% by adding water, followed by a 2.5 hr equilibration period. An impact mill was used to crack the kernel. The maize stock is dried in an air oven for 30 minutes at 66-71 °C. After cooling to 32 °C, the maize was sieved to separate the endosperm from the hull and germ fractions (US-3.5, US-5, US-10 sieves). The hull and germ fractions (on top of US-3.5 and US-5) are run again through the impact mill to loosen germ and excess endosperm from the hull. An aspirator or gravity table is used to separate the hull and germ fractions. The hull and germ fractions are sieved to remove fine endosperm particles. The endosperm portion of the maize kernel is separated by sieve sizes: the grit fraction is on top of the US-10 sieve, the meal fraction is on top of the US-62 sieve, and the flour fraction runs through the US-62 sieve. After milling and sieving the following fractions are obtained: hulls, germ, grits, meal and flour.

Oil processing: The germ fraction was dried in an air oven for 30 min at 104°C to 3% moisture content. The germ fraction is pressed to obtain crude oil from expeller and presscake from expeller. The residual oil in the presscake was solvent extracted with hexane in a steam jacketed, batch extractor at 63°C. Every 30 min for a period of 3 hrs, the hexane is drained and replaced by fresh solvent. Thereafter, the presscake is dried with warm air to remove remaining hexane, to obtain solvent extracted presscake. The hexane is removed from the extracts by evaporation, to obtain solvent extracted crude oil. During this procedure the oil reaches a temperature of 85 °C.

Oil refining: Crude oil from the expeller was refined in a laboratory oil refining machine. NaOH was added to the crude oil as specified by the amount of free fatty acid. The solution was mixed for 15 min at 20-24°C, followed by 12 min at 63-67°C. The neutralized oil was allowed to settle at 60-65° C. Thereafter the neutralized oil was refrigerated overnight (minimum 12 hrs) and the oil was filtered to obtain soapstock and refined oil.

Underlined samples were kept frozen at -23 °C or lower. Although storage time was not stated, maximum period is 344-568 d. The storage period for RAC samples is covered by the 2 year storage stability study on maize grain. Storage stability on processed maize commodities is covered by the 1 year storage stability study on maize meal and maize refined oil. Total phorate-related residues (oxidizable to phoratoxon sulfone) were determined by GC-FPD. Method M-1599 was used for grain, method M-1672 for oil and meal, method M-1706 for grits, flour, hulls, and press cake, method M-1724 for germ and method M-1734 for soapstock. The reported LOQ was 0.01 mg/kg eq for maize grain and 0.05 mg/kg eq for processed commodities. No method description and method validation report was available for each of the methods on processed commodities and accuracy of residue concentrations is therefore unknown. All samples were analysed on an as received basis.

Maize grain from these trials had been analysed shortly after harvest (within 29 d) and resulted in values of 0.036 mg/kg eq and 0.079 mg/kg eq for the low and high rate respectively (Roman, 1986: PA-730-062]. Maize grain values in Table 59 were obtained shortly before processing, and were similar to the earlier values. Results were not corrected for concurrent method recovery (80%-126% for all processed commodities), nor for matrix interferences (< 0.3 LOQ for all commodities, except hulls). Concurrent method recoveries for RAC were not verified. Due to matrix interferences, the LOQ for hulls was increased to 0.020/0.3=0.07 mg/kg eq. Mass fractions were not stated and therefore percentage transference could not be calculated and residue mass balance could not verified.

Table 59. Total phorate-related residues (oxidizable to phoratoxon sulfone) in processed commodities of field treated maize.

Location, year, (variety)	Form, kg ai/ha	DAT	Commodity	Total mg/kg eq	%M	P-factor	%T	Reference
Monticello, IL, USA; 1985 (T-1100)	200 G 1x 2.91 1x 2.91 1x 2.24	30	RAC hulls germ grits meal flour crude oil, expeller presscake, expeller crude oil, solv extracted presscake, solv extracted refined oil soapstock deodorized oil	0.036 0.30 < 0.05 < 0.05 0.052 < 0.05 0.056 < 0.05 0.081 < 0.05 0.073 < 0.05 < 0.05	-	- 8.3 < 1.4 < 1.4 1.4 < 1.4 1.6 < 1.4 2.2 < 1.4 2.0 < 1.4 < 1.4	-	Potts, 1986 [PA-730-042] Potts, 1987 [PA-730-041] [PA-730-039] [PA-730-034]
Monticello, IL, USA; 1985 (T-1100)	200 G 1x 7.29 1x 7.29 1x 5.60	30	RAC hulls germ grits meal flour crude oil, expeller presscake, expeller crude oil, solv extracted presscake, solv extracted refined oil soapstock deodorized oil	0.062 0.72 0.14 < 0.05 0.17 0.14 0.25 0.062 0.29 < 0.05 0.36 < 0.05 < 0.05	-	- 12 2.3 < 0.81 2.7 2.3 4.0 1.0 4.7 < 0.81 5.8 < 0.81 < 0.81	-	idem

Processing study on coffee beans

Study 1. A processing study was undertaken in which green coffee beans were sprayed with a phorate sulfone solution in acetone (Peterson, 1981: PA-790-020). Final concentration was 0.1 or 4.6 mg/kg eq. The sprayed beans were split in two portions. One portion was roasted at 260 °C for 5 to 6 minutes in an oven; the other portion was not treated. Beans were cooled and grinded.

Samples were stored frozen (temperature not stated). Storage time is not stated but is maximally 52 d. Storage stability studies on raw and processed coffee commodities have not been submitted and therefore accuracy of residue data is unknown. Samples were analysed for total phorate-related residues (oxidizable to phoratoxon sulfone) by GC-FPD, following method M-0684. The reported LOQ is 0.05 mg/kg eq for green and roasted coffee beans.

Results are shown in Table 51. Results were not corrected for concurrent method recoveries (70%-124% for RAC and roasted beans) nor for matrix interferences (< 0.3 LOQ for roasted beans). Due to matrix interferences, the LOQ for the RAC was increased to 0.025/0.3 = 0.09 mg/kg eq. Because processing was not carried out with incurred residues, no processing factors were calculated.

Study 2. A processing study was undertaken in which field treated coffee beans were roasted (Babbitt and Lesiewicz, 1984: PA-790-023). Green coffee beans were harvested from plots treated at an exaggerated rate. Harvested coffee beans were air dried for a period of 21 d. Sample sizes were not stated. Period and storage conditions between harvest and analysis were not stated. Green beans were roasted at 260 °C for 5 to 6 minutes.

Samples were stored frozen (temperature not stated). The storage period is not stated but is maximally 4 months. Storage stability studies on raw and processed coffee commodities have not been submitted and therefore accuracy of residue data is unknown. Samples were analysed for total phorate-related residues (oxidizable to phoratoxon sulfone) by GC-FPD, following Method M-0684. The reported LOQ is 0.02 mg/kg eq for green and roasted coffee beans.

Results are shown in Table 60. Results were not corrected for matrix interferences (< 0.3 LOQ for roasted beans). Because of matrix interferences, the LOQ for the RAC was increased to 0.008/0.3=0.03 mg/kg eq. Recoveries were not verified and therefore performance of the method at the time of sample analysis is unknown.

Table 60. Total phorate-related residues (oxidizable to phoratoxon sulfone) in processed commodities of spiked and field treated coffee.

Location, year, (variety)	Form, kg ai/ha	DAT	Commodity	Total mg/kg eq	%M	P-factor	%T	Reference
spiked at 0.1 mg/kg eq	-	-	RAC roasted beans	0.09^{a} $< 0.05^{a}$	-	-	-	Peterson, 1981 [PA-790-020]
spiked at 4.6 mg/kg eq	-	-	RAC roasted beans	4.60^{a} $< 0.05^{a}$	-	-	-	idem
Paulinia, Sao Paulo, Brazil, 1983 (Mundo novo)	50 G 80 kg ai/ha [b] (80 g ai/tree) (21 yr old)	160	RAC roasted beans	0.48 0.032 no recoveries	-	0.067		Babbitt and Lesiewicz, 1984, [PA-700-023]

a Average of three replicate analyses.

b. The dose rate is only given as g ai/tree. The present reviewer calculated dose rates from the assumption that 1 tree is 10 m^2 using the formula: [80 (g ai/tree) / 10 (m^2)] x 10 = 80 kg ai/ha.

Processing studies summary

In Table 61, valid processing factors for potato, maize and coffee commodities are summarised.

One potato study was considered unreliable because residues in the washed potatoes were higher than in the raw agricultural commodity. One maize study was considered unreliable because residues in the raw agricultural commodity (0.036 mg/kg) were lower than the practical LOQ (0.05 mg/kg) of the analytical method. These studies are not summarized below.

Table 61. Summary of valid processing factors on potato, maize and coffee.

commodity	Processing factors	Processing factor (median or best estimate)
Potato chips	< 0.07, < 0.3	< 0.07
Potato flakes	1.6	
Potato granules	1.2, 3.6	2.4
Washed potatoes	0.32, 0.49	0.405
Peeled potatoes	0.25, 0.28	0.265
Potatoes boiled with peel	0.13	
Potatoes boiled without peel	0.11	
Boiled potato peels	0.14	
Potatoes baked with peel	0.28	
Potatoes baked without peel	0.27	
Baked potato peels	2.4	
French fries	0.38	
Raw potato peels	0.52, 0.63, 0.73, 0.87	0.68
Dry potato peels	2.2	
Potatoes microwaved with peel	0.36	
Maize hulls	12	
Maize germ	2.3	

Maize grits	< 0.81	
Maize meal	2.7	
Maize flour	2.3	
Maize crude oil, expeller	4.0	
Maize presscake, expeller	1.0	
Maize crude oil, solvent extracted	4.7	
Maize presscake, solvent extracted	< 0.81	
Maize refined oil	5.8	
Maize soapstock	< 0.81	
Maize deodorized oil	< 0.81	
Roasted coffee beans	0.067	

It should be noted that in the dietary intake calculations for potato, processing data on French fries is used; the consumption data should be adjusted with a drying factor resulting from the frying process.

Residues in the edible portion of food commodities

No data submitted.

Residues in animal commodities

Direct animal treatments

Not applicable, because phorate is not registered for use on animals.

Farm animal feeding studies

The Meeting received information on feeding studies with calves, lactating cows and laying hens.

Cattle feeding studies

Study 1. A feeding study was conducted in 1961 in the USA, in which two groups of three Holstein calves were dosed at levels of 0 and 0.1 mg ai/kg bw for 14 consecutive days (Hill, 1961: PA-705-009). Dosages were administered in gelatin capsules; the way of administration was not stated. Calves were 6-8 months of age and weighted 220-234 kg (average 236 kg). Dosages as mg ai/kg feed were not stated. Calves were sacrificed and samples of thigh muscle, fat, liver and kidney were collected. The elapsed time between last dose and sacrifice was not stated. Samples were stored frozen (temperature and duration not stated). Storage stability studies on tissues have not been submitted and therefore accuracy of residue data is unknown.

In a preliminary dose-finding study, animals showed no signs of organophosphate poisoning at a dose rate of 0.1 mg ai/kg for 7 consecutive days followed by a dose rate of 0.2 mg ai/kg bw for 7 consecutive days. At dosages equivalent to 0.1 mg ai/kg bw, as in the final study, animals showed no significant differences in red blood cell acetylcholinesterase activity as compared to controls. When levels were increased to 0.2 mg ai/kg bw, animals showed significant depression of red blood cell acetylcholinesterase activity.

Total phorate-related residues (oxidizable to phoratoxon sulfone) were determined by their acetylcholinesterase inhibitive power in an electrometric acetylcholinesterase essay, method B. The reported LOQ of the method was 0.1 mg/kg eq for tissues.

Total phorate-related residues (oxidizable to phoratoxon sulfone) in tissues were all below the LOQ of 0.1 mg/kg eq. Samples were not corrected for concurrent method recovery (75%-127%), nor for matrix interferences (< 0.1 mg/kg eq).

Study 2. A feeding study was conducted in 1961 in the USA, in which three groups of three lactating Holstein cows were dosed at levels of 0, 0.05, and 0.1 mg ai/kg bw per day for 14 consecutive days (Hill, 1961: PA-705-009). Dosages were administered twice daily in gelatin capsules; the method of administration was not stated. Cows weighed 485-505 kg (average 493 kg); the age of the cows was not stated. Dosages as mg ai/kg of feed were not stated. Milk was sampled daily and a.m. and p.m. milkings were pooled. Tissues were not collected. Sample storage conditions were not stated and therefore accuracy of residue data is unknown.

Animals at both dose rates showed no significant differences in red blood cell acetylcholinesterase activity as compared to controls.

Total phorate-related residues (oxidizable to phoratoxon sulfone) were determined by their acetylcholinesterase inhibitive power in an electrometric acetylcholinesterase essay, method B. The reported LOQ of the method was 0.02 mg/kg eq for milk.

Total phorate-related residues (oxidizable to phoratoxon sulfone) in milk from the 0.05 mg ai/kg dose rate were all below the LOQ of 0.02 mg/kg eq. In samples from the 0.1 mg ai/kg dose residues were found (see Table 62). Samples were not corrected for concurrent method recovery (90%-105%), or for matrix interferences (< 0.02 mg/kg eq).

Table 62. Summary of total phorate-related residues (oxidizable to phoratoxon sulfone) in milk from cows dosed with 0.1 mg ai/kg bw/d.

Animal no	Day 1	Day 3	Day 7	Day 10	Day 14
	mg/kg eq	mg/kg eq	mg/kg eq	mg/kg eq	mg/kg eq
80	< 0.02	< 0.02	0.03	0.05	0.04
86	< 0.02	< 0.02	0.03	0.05	0.06
88	< 0.02	< 0.02	0.04	0.06	0.05
Mean	< 0.02	< 0.02	0.033	0.053	0.050

Study 3. In a US cattle feeding study, conducted in 1995, fourteen non-pregnant lactating Holstein cows were divided into three treatment groups (Leonard, 1995: PA-705-006 and PA-705-008). Cows were 3 to 8 years old in the weight range of 520-708 kg (average 602 kg). Animals in groups A (4 cows), B (4 cows), and C (6 cows) were dosed orally once a day for 28 consecutive days with gelatine capsules using a balling gun. Control animals received placebo capsules. For two cows of group C, a withdrawal period of up to 14 d was included. Chemical purity of the test substance was 91.8% ai. Using an average actual daily feed intake of 20 kg dry matter/d, mean actual dosages were calculated to be equivalent to 0, 1.39 and 3.21 mg ai/kg dry feed. Actual dosages ranged from 1.17-1.83 mg ai/kg feed and 2.63-4.18 mg ai/kg feed for individual cows from group B and group C, respectively. Dosages as mg ai/kg bw were not stated.

In a preliminary dose-finding study, animals showed severe signs of organophosphate poisoning (diarrhoea, stiffness, muscular tremors) at dosages equivalent to 14 mg ai/kg dry feed, and mild signs of organophosphate poisoning (depression, salivation, off feed consumption) at dosages equivalent to 7 and 5 mg ai/kg dry feed. At dosages equivalent to 1.39 and 3.21 mg ai/kg dry feed, as used in the final study, animals showed no signs of organophosphate poisoning.

Milk samples were collected each day and p.m. and a.m. milkings were pooled. Animals were sacrificed within 20 hrs of the last dose and samples of loin muscle, omental fat, both kidneys and whole liver were collected. Samples were stored at -20 °C for 15-46 d for milk or 12-27 d for tissues. The storage period for milk is covered by the 18 months storage stability study; storage stability data for tissues are not required as the storage period is shorter than 30 d and there is no indication of instability of residues from the milk stability study. Two cows from group C (withdrawal cows) were not sampled for milk and were not sacrificed. Total phorate-related residues (oxidizable to phoratoxon sulfone) were determined following method M-2461 in tissues and M-2469 in milk samples (from day

2, 4, 5, 6, 7, 8, 10, 12, 15, 17, 20, 23, 26, 28). The reported LOQ of the methods were 0.02 mg/kg eq for animal tissues and 0.005 mg/kg eq for milk samples.

Cows from groups A, B, and C showed total that phorate-related residues (oxidizable to phoratoxon sulfone) were below the LOQ of < 0.005 mg/kg eq for whole milk (day 2 to day 28) or < 0.02 mg/kg eq for tissues. Samples were not corrected for concurrent method recovery (74%-124% for milk; 83%-129% for tissues), nor for matrix interferences (< 0.3 LOQ).

Poultry feeding study

A feeding study was conducted in 1969 in the USA, in which four groups of six laying hens were dosed at levels of 0, 0.1, 0.3 and 1.0 mg/kg feed as total phorate (1:1 phorate: phoratoxon sulfone) for 21 consecutive days (Higham, 1969: PA-705-001). Dosages were administered as solutions in water by gavage. The weight of the hens was approximately 3.17 kg each. The breed and age of the hens was not stated. Dosages were calculated, assuming a daily dry matter intake of 150 g/bird. Dosages as mg ai/kg bw are not stated. A composite egg sample from each group was collected only on the final day of treatment. The hens were sacrificed 2 to 3 hrs after final dosing and muscle, fat, liver and kidney were collected. Tissues from two birds were combined to make one sample. Sample storage conditions were not stated and therefore accuracy of residue data is unknown.

Total phorate-related residues (oxidizable to phoratoxon sulfone) were determined following GC with a caesium bromide thermionic detector, method D. The reported LOQ of the method was 0.05 mg/kg eq. Because of matrix interferences, the LOQ for fat was increased to 0.06 mg/kg eq (see methods section).

Total phorate-related residues (oxidizable to phoratoxon sulfone) in tissues and eggs were all below the LOQ of 0.05 mg/kg eq. Samples were not corrected for concurrent method recovery (78%-114% for eggs, 63%-125% for tissues), nor for matrix interferences (< 0.3 LOQ, except fat up to 0.019 mg/kg eq).

RESIDUES IN FOOD IN COMMERCE OR AT CONSUMPTION

Phorate was included in the list of analytes examined in the foods in the 20th Australian Total Diet Survey (FSANZ, 2003). Phorate was not found in any sample of food analysed (limit of detection 0.01 mg/kg).

The Pesticide Data Program (PDP) of the USA Department of Agriculture (USDA) collects data on pesticide residues in food (USDA, 2002). Table 63 summarises the data for phorate and its metabolites in the PDP database. The data represent results of monitoring of pesticide residues in food up to the year 2002.

Table 63. Monitoring data for phorate from the USA Pesticide Data Program (PDP).

Compound	Commodity	Total Samples Screened	Samples with Detection	% Samples with Detection	Range of values found (mg/kg)	Range of LOQs (mg/kg)
Phorate	Apples	556	0			0.005 – 0.014
	Asparagus	622	0			0.004 – 0.11
	Bananas	638	0			0.005 – 0.014
	Broccoli	125	0			0.011
	Carrots	536	0			0.002 – 0.011
	Celery	170	0			0.001 – 0.011
	Cucumbers	129	0			0.005
	Mushrooms	642	0			0.002 – 0.011
	Peaches	563	0			0.002
	Pineapples	360	0			0.006 – 0.011

Compound	Commodity	Total Samples Screened	Samples with Detection	% Samples with Detection	Range of values found (mg/kg)	Range of LOQs (mg/kg)
	Potatoes	370	0			0.011 – 0.012
	Spinach	363	0			0.012
	Sweet bell peppers	186	0			0.002
	Sweet corn, canned/frozen	727	0			0.011 – 0.012
	Sweet peas, canned/frozen	643	0			0.004 – 0.011
	Total	6,630	0			
Phoratoxon	Carrots	392	0			0.001
	Mushrooms	516	0			0.001
	Peaches	563	0			0.001
	Sweet Bell Peppers	186	0			0.001
	Total	1,657	0			
Phorate sulfoxide	Apples	433	0			0.020
	Bananas	321	0			0.020
	Carrots	392	0			0.004 – 0.009
	Mushrooms	516	0			0.004 – 0.009
	Peaches	563	0			0.004 – 0.009
	Sweet bell peppers	186	0			0.009
	Total	2,411	0			
Phorate sulfone	Apples	556	0			0.004 – 0.015
	Asparagus	623	0			0.004 – 0.12
	Bananas	638	0			0.004 – 0.015
	Broccoli	125	0			0.004
	Carrots	536	0			0.002 – 0.004
	Celery	170	0			0.002 – 0.004
	Cucumbers	129	0			0.004
	Mushrooms	642	0			0.002 – 0.004
	Peaches	563	0			0.002 – 0.003
	Pineapples	360	0			0.004 – 0.017
	Potatoes	370	2	0.5	0.007 – 0.040	0.004 – 0.024
	Spinach	363	0			0.024
	Sweet bell peppers	186	0			0.003
	Sweet corn, canned/frozen	727	0			0.004 – 0.012
	Sweet peas, canned/frozen	643	0			0.004 - 0.012
	Total	6,631	2			
Phorate sulfoxide	Apples	433	0			0.020
	Bananas	321	0			0.020
	Carrots	392	0			0.004 – 0.009
	Mushrooms	516	0			0.004 – 0.009
	Peaches	563	0			0.004 – 0.009
	Sweet bell peppers	186	0			0.009
	Total	2,411	0			

APPRAISAL

Phorate is a systemic organophosphate contact insecticide and acaricide that inhibits acetyl cholinesterase activity. Residue and analytical aspects of phorate were evaluated by the JMPR in 1977, 1984, 1990, 1991, and 1992. The 30th Session of CCPR (1998) requested priority scheduling of a full review of the compound because of acute intake concerns. Phorate was listed in the Periodic Re-Evaluation Programme at the 36th Session of the CCPR for periodic review by 2005 JMPR. The JMPR toxicological review was conducted in 2004, which established an ADI of 0-0.0007 mg/kg bw and an ARfD of 0.003 mg/kg bw.

Information on the latest GAP, residue data, metabolism, analytical methods, storage stability and processing studies were provided by the manufacturer to enable the assessment of existing and proposed MRLs on a number of crops or crop groups, including beans, potatoes, sugar beet, sweet corn, maize, sorghum, cotton, and coffee.

In addition, GAP information and/or national MRLs were supplied by Australia and The Netherlands.

The following common names were used for the metabolites discussed below:

phorate sulfoxide	*O,O*-diethyl S-ethylsulfinylmethylphosphorodithioate
phorate sulfone	*O,O*-diethyl S-ethylsulfonylmethylphosphorodithioate
phoratoxon	*O,O*-diethyl S-ethylthiomethylphosphorothioate
phoratoxon sulfoxide	*O,O*-diethyl S-ethysulfinylmethylphosphorothioate
phoratoxon sulfone	*O,O*-diethyl S-ethylsulfonylmethylphosphorothioate

Animal metabolism

The Meeting received information on the fate of orally dosed phorate in lactating goats and laying hens. Phorate was ^{14}C labelled at the methylene position.

Studies on laboratory animal metabolism (rats) were evaluated by the WHO panel of the 2004 JMPR. It was reported that after oral administration of radiolabelled phorate to rats, 77% of the administered dose was recovered in the urine within 24 h after dosing. Faecal excretion accounted for approximately 12% of the administered dose. Over the total duration of the study (192 h), effectively the entire administered dose was eliminated by excretion. The bulk of the administered dose (94%) was biotransformed to nonphosphorylated metabolites. The metabolic pathway responsible for the formation of these metabolites resulted from the cleavage of the phosphorus-sulfur bond, methylation of the liberated thiol group and oxidation of the resulting divalent sulfur moiety to the sulfoxide and sulfone. Thus, these studies demonstrated that in rats phorate is rapidly absorbed and excreted and the accumulation of any toxicologically significant residue is not of concern.

In two consecutive studies, lactating goats were orally treated (balling gun) with ^{14}C-labelled phorate at dose rates of 1.35 and 5.40 ppm in the feed for either 3 or 7 days. At the highest dose, significant depression in plasma cholinesterase activity was observed. Recovery of total applied radioactivity (in excreta, tissues, milk) was not investigated. After 3 days of treatment, the highest concentration of radioactive residues was found in the liver (0.62 mg/kg eq). Kidney, milk, muscle and fat contained 0.41, 0.26, 0.19, < 0.05 mg/kg eq, respectively. After 7 days of treatment, concentration levels in liver, kidney, milk, muscle and fat were 0.90, 0.76, 0.50, 0.64, and 0.21 mg/kg eq, respectively (all results from highest dose level). Residue levels in milk increased steadily and no plateau was reached during both the dosing periods.

Approximately 95% to 99% total radiolabelled residue (TRR) in extracts of milk, liver, kidney, leg muscle, tenderloin muscle, and omental fat was composed of non-phosphorylated metabolites, which resulted from cleavage of the phosphorus-sulphur bond and the methylation of the resultant mercaptan. The major metabolite in all tissues and milk was, ethylsulfonyl methylsulfonyl methane accounting for 94% to 99% TRR in the tissues and milk. The remaining radioactivity was composed of the parent compound and its various oxidative products (< 0.01% to 2.2% TRR). In the 3 days experiment (highest dose level) the toxicologically significant compounds parent, phorate sulfone and phorate sulfoxide were found at very low levels: milk contained 0.052 µg/kg eq parent and 0.39 µg/kg eq phorate sulfoxide, liver contained 4.34 µg/kg eq parent, kidney 2.50 µg/kg eq phorate sulfoxide, muscle 0.019 µg/kg eq parent, 0.077 µg/kg eq phorate sulfone and 0.14 µg/kg eq phorate sulfoxide, and fat contained none of those at a detectable level.

Groups of laying hens were orally treated (gelatine capsules) for 5 days with ^{14}C-labelled phorate at dose rates of about 1 and 3 ppm in the feed. Recoveries of the administered doses averaged 64−66%: 62−64% of the total administered radioactivity in excreta, 0.7−1.5% in eggs, 0.5%-0.8% in organs and 1.2% in carcass. Fortification of control excreta with ^{14}C-phorate resulted in a recovery of 78% after 24 h at room temperature. These results suggest that the low but consistent overall recovery may be associated with the volatility of phorate and/or the low molecular weight of the metabolic products.

Liver and kidney were found to contain the highest level of radioactive material. At the highest dose level, the amounts were 0.31 and 0.24 mg/kg eq respectively. At this dose level total radioactive residues in breast muscle, skin/fat, egg white and egg yolk amounted to 0.031, 0.047, 0.048−0.10, and 0.017−0.20 mg/kg eq respectively. Residue levels in egg yolks and whites increased steadily and no plateau was reached during the dosing period.

Metabolites found in the tissues and eggs include ethylsulfonyl methylsulfonyl methane; (ethylsulfinyl)methyl methyl sulfone; ethyl (methylsulfinyl)methyl sulfone. One additional non-phosphorylated metabolite, ethylsulfinyl methylsulfinyl methane was also found in the egg white. Neither the parent compound phorate, nor any of the oxidative metabolites phorate sulfoxide, phorate sulfone, phoratoxon, phoratoxon sulfoxide or phoratoxon sulfone was found in tissues or in eggs. Significant fractions of the radioactive residues in tissues and eggs (47−59% TRR) were unextractable but were released by enzyme hydrolysis with protease. Since the released activity was highly polar, it was concluded not to derive from any of the phorate oxidative metabolites.

In conclusion, the metabolism of phorate in farm animals was similar to that in laboratory animals. Goats and laying hens dosed with phorate quickly detoxify the compound through a set of oxidative, toxic, metabolites. Neither parent nor any of its oxidative metabolites accumulate in edible tissues, milk and eggs.

Plant metabolism

The Meeting received information on the translocation and metabolism of phorate in plants placed in a phorate emulsion, in cotton grown from seeds treated with phorate, and in various plants after soil or foliar application of phorate. Characterization of metabolites was limited to root and foliar parts of young or immature plants. Confined rotational crop studies gave information on the metabolite composition of mature crops (see environmental fate section). Experiments were carried out with ^{32}P labelled phorate or with phorate ^{14}C labelled at the methylene position.

The roots of red kidney bean seedlings were placed in an emulsion of ^{32}P-phorate for 1 day and transplanted afterwards. Leaves were analysed 1, 4 and 12 days after treatment. The bases of young_cotton plants, lemon seedlings and alfalfa seedlings were treated with a topical application of ^{32}P-labelled phorate solution. At various intervals after application (up to 14−17 days) the upper leaves were removed. In all experiments, radioactive residues translocated to the leaves. In red kidney bean leaves analysed 1, 4 and 12 days after application the primary metabolites were phorate sulfoxide and/or phorate sulfone, which could not be separated on the columns used. Small amounts of phoratoxon sulfoxide and/or phoratoxon sulfone and unchanged phorate were also found. No phoratoxon was found. The hydrolysis products formed were phosphoric acid, the diethyl esters of phosphoric acid, phosphorothioic acid and phosphorodithioic acid. Parent and the same four metabolites were also identified in a chloroform extract of cotton, lemon and alfalfa leaves (day 1−17). For cotton leaves, parent was found up to 5 d and never exceeded 5% of the radioactivity. Phorate sulfoxide reached a maximum of 85% of the radioactivity at day 1 after application and thereafter decreased to 35% at day 14. Phorate sulfone, phoratoxon sulfoxide and phoratoxon sulfone increased with time at up to 35%, 15% and 10% radioactivity at day 14, respectively. Phoratoxon was not found at any time point.

A mixture of ^{32}P-phorate and charcoal was coated on cotton seeds wetted with 2% methylcellulose at a concentration of 160 kg ai/t or 320 kg ai/t. Treated seeds were planted and cotton plants were sampled at 3.9, 7.4, 10.7 or 16 weeks after planting. In addition, foliage from cotton plants grown for 2 weeks from treated seed was sampled for identification of metabolites. Total ^{32}P residues were less than 0.03 mg/kg eq in leaves and seeds maturing from plants grown from seed treated with 320 kg ai/t at 16 weeks after planting. The residues isolated from the foliage consisted of phorate sulfoxide and phorate sulfone (ratio 61:39) and phoratoxon sulfoxide and phoratoxon sulfone (ratio 70:30). The parent itself was not identified because of interference from plant pigments. Phoratoxon was not found.

Beans, beets, cabbage, carrots, lettuce and peas were treated with radiolabelled ^{32}P-phorate using both a foliar and a soil application. Applications were made with an EC formulation at a rate of 1.12 kg ai/ha. The vegetable foliage was sampled at 2 hrs and 1, 2, 4, 8, 17 and 32 DAT. In addition pea plants were soil treated and the foliage was sampled at 14 DAT for identification of metabolites. Average values of the distribution of ^{32}P radioactivity and anti-cholinesterase activity in pooled extracts from beans, beets, cabbage, carrots, lettuce and peas were determined. Anti-cholinesterase activity increased when P=S was replaced by P=O, and increased further upon successive oxidation to sulfoxide and sulfone. Anti-cholinesterase activity increased for about the first four days and then declined but the presence of anti-cholinesterase activity persisted for 20 to 30 days. Residues became more polar in time, showing detoxification of the oxidative metabolites. The residues isolated from the pea foliage consisted of phorate sulfoxide and phorate sulfone (ratio 80:20). Parent itself was not identified because of interference from plant pigments. Phoratoxon was not found.

The translocation and metabolism of ^{14}C-phorate in maize seedlings, planted in treated test soil (sandy soil), was investigated. After 18 days, 77% of the applied radioactivity was recovered: 71% in soil, 4.0% in maize greens and 1.8% in maize roots. Phorate sulfoxide, phorate sulfone and phoratoxon sulfoxide were the only compounds found in extracts from maize greens; no phorate, phoratoxon or phoratoxon sulfone was found. In nine supervised field trials on maize and sweet corn where phorate was banded at planting and at cultivation, the main metabolites in forage and fodder again were phorate sulfone and phorate sulfoxide. Incidentally parent, phoratoxon, phoratoxon sulfoxide and phoratoxon sulfone were also found.

The translocation and metabolism of ^{14}C-phorate in oat seedlings, planted in either treated silt loam soil or sandy soil, were investigated. After 13 days, for the sandy soil system 59% of total applied radioactivity was recovered: 26% in soil, 3.5% in roots and 30% in oat greens. For the silt loam soil system 76% of total applied radioactivity was recovered: 68% in soil, 0.5% in roots and 7.4% in oat greens. Although these results do not correspond to those of the maize experiment described above, they seem to indicate that the translocation of ^{14}C-phorate to the oat seedlings depends on the soil type, where uptake and translocation is more efficient in sandy soils. Phorate sulfoxide and phorate sulfone were the major compounds present in oat greens and roots; the remainder was unknown compounds.

A great difference in the nature of ^{14}C residues was found between carrots and the other two root crops when extraction efficiency was tested for potatoes, carrots and radishes, which were soil treated with ^{14}C-phorate. Plants were grown from seeds (or seed potatoes) in pots in a silt loam soil. When plants began to produce edible portions, an aqueous suspension of ^{14}C-phorate was pipetted onto both the soil and the partly exposed roots/tubers at an application rate equivalent to 2.25–3.35 kg ai/ha. Roots/tubers were harvested 5, 10, and 15 days after treatment (DAT). Total recovered radiolabelled (^{14}C) residues in the roots/tubers ranged from 0.86 to 12.6 mg/kg eq. With carrots, more than 96% of the radioactivity was extractable with organic solvent, and the ratio of water soluble to organic solvent soluble ^{14}C residues did not increase with increasing incorporation time. With potatoes and radishes, the ratio of water soluble ^{14}C residues was much greater than with carrots and this ratio increased with time, while that of carrots remained constant. Phorate sulfoxide (20-75%) and phorate sulfone (15–70%) were the major compounds present in dichloromethane extracts from potatoes and radishes; parent (10–25%), phorate sulfoxide (50–60%) and phorate sulfone (10–25%) were the major compounds present in the dichloromethane extracts from carrots (expressed as % ^{14}C in dichloromethane extracts). Phorate and phorate sulfoxide decreased with time, while phorate sulfone increased with time. Phoratoxon, phoratoxon sulfoxide and phoratoxon sulfone were found at trace levels (< 3.2% of ^{14}C in dichloromethane extract). The six phorate residues accounted for 99% of ^{14}C in dichloromethane extracts of all three crops.

Effects of light intensity and temperature on the translocation and metabolism, in oat, pea, and maize plants, of ^{14}C-phorate in soil treated were investigated. Higher temperatures caused in most cases an increase in the uptake of ^{14}C compounds from soil. Higher light intensity also affected the metabolism of translocated ^{14}C compounds but primarily at 28°C. The relative distribution of benzene-soluble, water-soluble and unextractable radiocarbon was quite similar in all plants under all experimental conditions. Phorate sulfoxide was the major compound present in plant tops and soil. Contrary to soils, parent was not found in plant tops. Further compounds found in plant tops and soils were phorate sulfone, phoratoxon sulfoxide and phoratoxon sulfone.

In conclusion, when phorate is applied to the soil, it and its' degradates are taken up by the plants and translocated. When absorbed by plants, phorate is first oxidized at the thioether sulfur to form the phorate sulfoxide and sulfone and is then oxidized at the thiono sulfur to form the phoratoxon sulfoxide and sulfone. These oxidation products have a similar anticholinesterase activity as the phorate precursor and persist in plants for relatively long periods of time.

Environmental fate in soil

The Meeting received information on laboratory soil degradation and field and confined rotational crop studies. Experiments were carried out with phorate ^{14}C labelled at the methylene position.

Aerobic soil degradation studies showed that in soil, phorate degrades to phorate sulfoxide which in turn converts to phorate sulfone. Phorate degrades rapidly, while phorate sulfoxide degrades more slowly and phorate sulfone is the most persistent of the three. The half-life of phorate in sandy loam was estimated to be 3 days, while that of phorate sulfoxide was 75 days. The half-life of phorate sulfone could not be determined due to experimental difficulties.

From three confined accumulation studies in which maize, beetroot, lettuce, spring wheat, radish, carrots, peas and barley were grown at several time intervals after treating the soil with phorate (^{14}C labelled at the methylene position) the following conclusions could be drawn. A decrease of residue levels in soil was seen over time. Most of the radioactivity remained in the top 7.5 cm of soil, indicating that phorate and its metabolites exhibited no appreciable leaching beyond a 15 cm depth of soil. Phorate was rapidly oxidized in the soil and was converted into phorate sulfone. Only 0.2% TRR parent was found in the soil extract one month after treatment. Other metabolites identified in soil were phorate sulfoxide, phoratoxon, phoratoxon sulfoxide, phoratoxon sulfone and ethylsulfonyl methylsulfonyl methane.

In a field rotational crop study, radishes and carrots were planted in either a sand or a muck soil. The soil was treated with phorate at a rate of 3.4 kg ai/ha. The crops were planted either immediately after or one year following treatment. Radishes and carrots were harvested 4 and 14 weeks after planting, respectively. Greater conversion of phorate to phorate sulfoxide and phorate sulfone occurred in the muck soil as compared to the sand. More than 99% and 98% of the applied phorate and its oxidation products disappeared from the sand and muck soil, respectively, within a year of treatment. Low amounts of phorate sulfoxide and phorate sulfone (0.04 – 0.18 mg/kg eq) were found in radishes grown on both soils in the first year. No residues were present in the second year. No residues were found in carrots grown on either soil in the first year.

Soil residues consisting of phorate sulfone and predominantly non-toxic polar components can be taken up by rotational crops. However phorate applied at a rate of 3.8 kg ai/ha did not lead to the accumulation of phorate and its phosphorylated metabolites in following crops at a plant-back interval of 4 months after treatment (MAT). The assimilated phorate-derived residues are extensively metabolized by plants via non-phosphorylated metabolites to single carbon units, which subsequently are incorporated into endogenous cell components.

Environmental fate in water-sediment systems

The hydrolysis of ^{14}C-phorate, ^{14}C-phorate sulfoxide, and ^{14}C-phorate sulfone in sterile buffer systems was investigated under laboratory conditions. The hydrolysis half-lives of phorate at 25°C were estimated to be 2.36, 2.47, and 2.08 days, for pH 5, 7, and 9 respectively. The major degradate (maximum 31–87% of the total administered radioactivity at termination) observed in all treatments was formaldehyde. Phorate sulfoxide (maximum 5.2–6.6% of the total administered radioactivity at day 1) was formed only at pH 5. The results show that phorate will degrade under abiotic conditions and is not expected to persist in aquatic systems.

Hydrolysis of phorate sulfoxide and phorate sulfone occurs more slowly. At 25°C, hydrolysis half-lives were estimated to be 185, 118, and 7.02 days for phorate sulfoxide and 77.1, 60.2, and 5.25 days for phorate sulfone at pH 5, 7, and 9 respectively. The degradation pathway of phorate sulfoxide and phorate sulfone was pH-dependent at elevated temperatures with de-esterification being the predominant reaction at pH 5-7.

Methods of analysis

The meeting received descriptions and validation data on methods of residue analysis for enforcement and for residue methods used in the various study reports.

The Pesticide Analytical Manual (PAM) Volume II lists ten methods (1963-1973) for the enforcement of MRLs for phorate residues in/on plants and animal commodities. The description of method I, IA, IB was submitted to the present Meeting. Method I is based on the extraction of the parent and its oxygenated metabolites phorate sulfoxide, phorate sulfone, phoratoxon, phoratoxon sulfoxide and phoratoxon sulfone. The extracts are cleaned-up by liquid-liquid partitioning or alumina column chromatography. Phorate-related residues are oxidized to the common moiety metabolite, phoratoxon sulfone, using 3-chloroperoxybenzoic acid. The oxidized product is then analysed by GC with a phosphorus specific detector.

Method I was validated for animal commodities (milk, meat, fat, offal). Milk, meat and offal are extracted with chloroform, fat is extracted with acetonitrile. The oxidation of phorate to phoratoxon sulfone is about 70% complete. Because of this, parent recoveries are based on oxidized phorate, while phoratoxon sulfone recoveries are based on phoratoxon standards. Recoveries from milk samples resulted in 75–85% for the parent compound at 0.02 mg/kg eq and 95–103% for phoratoxon sulfone at 0.04 mg/kg eq. The reported LOQ was 0.01 mg/kg eq for milk and 0.02 mg/kg eq for meat tissues (cattle, goat, hogs, horses and sheep). *Method IA* was validated for cottonseed and safflower seed. Validation results are not available. *Method IB* was validated for sugar beets with a reported LOQ of 0.1 mg/kg eq. This method is considered an identification method in case a confirmatory analysis is required.

Phorate and its five metabolites (phorate, phorate sulfoxide, phorate sulfone, phoratoxon, phoratoxon sulfoxide, and phoratoxon sulfone) were taken through the USA FDA multiresidue method protocols described in PAM Volume I with some success. Protocols C and D gave satisfactory results.

Based on the information available it is unknown what LOQs are achievable for plant products in an enforcement situation. Based on existing CXLs and the available supervised residue trial data, it is assumed that an LOQ of 0.05 mg/kg is a practical value.

Residues in very early residue studies (1961–1963) were analysed by their cholinesterase inhibitive power in an electrometric cholinesterase assay. However, these assays are non-specific. Further, in one of those methods (method A) there is no correlation between total phorate-related residue concentration and cholinesterase activity. Residues with higher cholinesterase activity than oxidized phorate will give an erroneously high residue concentration, whereas compounds with lower cholinesterase activity than oxidized phorate will give an erroneously low residue concentration. This assay is therefore considered inaccurate for the purposes of undertaking residue analyses.

From 1971 on, analytical methods based upon gas chromatography with flame photometric detection (GC-FPD) for determination of total phorate-related residues (oxidizable to phoratoxon sulfone) have been developed for a wide range of substrates. The methods are based on the extraction of the parent and its oxygenated metabolites phorate sulfoxide, phorate sulfone, phoratoxon, phoratoxon sulfoxide and phoratoxon sulfone with either methanol-dichloromethane (10-90; plants) or acetonitrile (animal commodities). The extracts are cleaned-up and phorate-related residues are oxidized to the common moiety metabolite, phoratoxon sulfone, using 3-chloroperoxybenzoic acid in dichloromethane. The reaction mixture is cleaned-up by washing with sodium sulfite and bicarbonate solutions in water, precipitation of oily/fatty residues with aqueous ammonium chloride-phosphoric acid solution and water-dichloromethane partitioning. The dichloromethane is removed and the residue is redissolved in acetone, which is then analysed by GC-FPD in phosphorus mode. GC conditions: packed column 3% OV-210 on Supelcoport 80/100 mesh deactivated with Carbowax 20M at 155–200°C. Calibration is performed by running phorate standards through the oxidation procedure (analysed as phoratoxon sulfone). Oxidation efficiency is verified against a phoratoxon sulfone reference standard and should be at least 50% to start the analysis procedure.

The methods vary in the extraction solvent, in the clean-up procedures used before and after oxidation and in the GC-column conditions. The LOQ for most of the reported trials was 0.05 mg/kg eq. The methods have in general been validated on a wide range of substrates. However, most of the methods were validated with only a limited number of recovery samples per concentration level ($n < 5$), of compounds used for recovery checks (phorate and 5 oxidized metabolites), and/or of control samples analysed ($n < 2$). Alternatively calibration data was lacking.

Stability of pesticide residues in stored analytical samples

The Meeting received data on the stability of residues in dry beans, potatoes, sugar beets and maize stored frozen. In addition, the Meeting received data on the stability of residues in milk stored frozen.

Total phorate-related residues (oxidizable to phoratoxon sulfone) are stable for at least two years in dry bean, potato tuber, sugar beet roots and tops, maize grain, green maize plants, and maize straw samples when stored frozen at approximately -10°C to -20°C. In maize meal and maize refined oil stored at ≤ -23°C total phorate-related residues are stable for at least one year.

No storage data are available on green beans (seeds, seeds with pods). However, storage data for sugar beet tops or green maize forage/fodder (see below) may be extrapolated to green beans (seeds, seeds with pods). Storage data for cotton dry fodder were unavailable as well but the results for dry maize fodder may be extrapolated to cover this.

Storage stability data on cotton seed, coffee beans and on processed potato commodities were not available. The Meeting decided that given the results discussed above, it was highly unlikely that total phorate-related residues were unstable in these commodities.

Total phorate-related residues are stable in cows' milk for at least 4 days when stored in the refrigerator and at least 18 months when stored in the freezer at -20°C or lower. No storage data was submitted on tissues (poultry, ruminants) and eggs. Ruminant tissues from a cow feeding study were stored for less than one month and therefore storage data on these tissues are not needed. However, storage data on poultry tissues and eggs is lacking.

Definition of the residue

In animals, phorate is quickly detoxified and neither parent nor any of its oxidative metabolites accumulate in edible tissues, milk and eggs. The major metabolite in all tissues, milk and eggs was ethylsulfonyl methylsulfonyl methane. Nevertheless, phorate-related residues can be found at low levels.

When absorbed by plants, phorate is first oxidized at the thioether sulfur to form the phorate sulfoxide and sulfone and is then oxidized at the thiono sulfur to form the phoratoxon sulfoxide and sulfone. These oxidation products are all similar anticholinesterase agents to the phorate precursor and persist in plants for relatively long periods of time. In most cases, parent itself is present at low levels, but the ratio of the different metabolites changes from crop to crop.

The analytical methodology available relies on the oxidation of all phorate-related residues to the common moiety metabolite, phoratoxon sulfone. Supervised residue trials show that total phorate-related residues (oxidizable to phoratoxon sulfone) are not to be expected in edible crops, except in potatoes. The composition of the residue in potato tubers after application according to GAP is unknown.

Considering all of the above, the Meeting decided that the residue definition for phorate, both for enforcement and for risk assessment for animal and plant commodities, is:

Sum of parent, its oxygen analogue, and their sulfoxides and sulfones, expressed as phorate.

Although the parent compound has a log K_{ow} of 3.92, animal metabolism studies indicate that the total residue is not fat-soluble.

Results of supervised trials on crops

Supervised residue trials were available for fruiting vegetables (sweet corn), legume vegetables (green beans, green snap beans), pulses (dry beans, dry soya beans), root and tuber vegetables (potato, sugar beet), cereals (maize, sorghum), oilseeds (cotton), and coffee. Supervised trials on the remaining commodities that currently have a CXL were not provided. Therefore the Meeting decided to withdraw the current recommendations for fodder beet, peanut, peanut oil crude, peanut oil edible, and wheat.

In situations where residues from supervised trials at GAP show **nil** residues, the MRL was chosen to reflect a sensitivity that is compatible with enforcement activities. Where two different LOQs apply to the residue data, the lowest value was chosen only if the above was true. In this case the lower LOQ will be taken to represent the STMR. The HR value would then be recommended at the highest LOQ used in the studies unless a majority of the observations were derived from the more sensitive LOQ.

In situations where residues from supervised trials at GAP show **nil** residues even at exaggerated rates, then the MRL will still be chosen to reflect an LOQ that is compatible with enforcement activities. However, both the STMR and HR values will be set at zero.

Sweet corn (corn-on-the-cob)

Nine trials were reported on sweet corn from the USA. No trials were according to GAP of the USA (1.1–1.5 kg ai/ha, PHI 30 days). In the trials Phorate granular formulation was either applied as a single application in a band at planting or as a double application: one in a band at planting followed by a band at cultivation. Rates per application ranged from 1.46 to 7.29 kg ai/ha, with sampling occurring 37–74 days after treatment.

The Meeting decided that there was insufficient data to estimate a maximum residue level for sweet corn (corn-on–the-cob) and decided to withdraw the current recommendation of 0.05 mg/kg.

Legume vegetables

Eighteen trials were reported from the USA. Four trials on green bean seeds (without pods), four trials on green bean pods (with seeds) and ten trials on snap bean pods (with seeds) were reported. At planting, the phorate granular formulation was either drilled to the side of the seed or banded over the row using a granular applicator at application rates between 1.68–4.70 kg ai/ha. Two of the trials on green bean seeds were according to USA GAP (1.1–2.3 kg ai/ha, PHI 60 days) and total phorate-related residues were < 0.05 (2) mg/kg eq. However, these trials could not be used since residues were measured in the beans without pods. The ten snap bean pod trials were all within GAP, albeit with a shorter PHI (48–52 days). All residues were < 0.05 mg/kg eq.

Although the analytical method used in these trials (Method M-1718**)** was not ideal for green beans, because of low recoveries at 0.05-0.10 mg/kg eq (< 70%) and high relative standard deviation (RSD_r) at 0.01 mg/kg eq (> 20%), the Meeting decided to use the results as no actual residues were measured or expected.

The Meeting agreed to withdraw the previous maximum residue level recommendation for common bean (pods and/or immature seeds) (0.1 mg/kg), to be replaced by a recommendation of 0.05* mg/kg. The Meeting estimated an STMR of 0.05, and a HR of 0.05 mg/kg for phorate on common beans (green pods and/or immature seeds).

Pulses

Dry beans

Twenty-three trials on dry harvested beans were available from the USA. The phorate granular formulation was applied at a rate of 2.0 to 4.7 kg ai/ha in furrow, as a band over the row, or drilled to the side of the seed at planting. In all trials total phorate-related residues were < 0.05 mg/kg eq, except for trials PA-720-010 and PA-720-011, where the actual LOQ was 0.06 mg/kg eq because of matrix interference.

Four of the trials were according to USA GAP (1.1-2.3 kg ai/ha, PHI 60 days) and total phorate-related residues were < 0.05 mg/kg eq. In four other trials where a twofold exaggerated dose was applied (4.7 kg ai/ha) total residues were also < 0.05 mg/kg eq.

The Meeting estimated a maximum residue level of 0.05* mg/kg, and an STMR of 0.05 mg/kg for phorate on dry beans.

Soya bean (dry)

Twenty eight trials on soya beans were available from the USA. At planting, the phorate formulation was applied as a side band in furrow, in a band, or drilled to the side of the seed, at rates of 1.1 to 9.4 kg ai/ha.

None of the trials were according to GAP of the USA (1.7 kg ai/ha, PHI not specified). In four trials rates were below GAP while the remainder were in excess of GAP. However, even at a rate of 9.4 kg ai/ha, total phorate-related residues were < 0.05 mg/kg eq.

The Meeting estimated a maximum residue level of 0.05* mg/kg, and an STMR of 0 mg/kg for phorate on soya beans, dry.

Potatoes

Ware potatoes are normally harvested within 90–120 days after planting. Early maturing varieties can be harvested before 90 days, while late maturing ones (such as Russet Burbank or Maris Piper varieties) are usually harvested after 120 days. The PHI therefore depends on the crop variety. Although on many labels a PHI of 90 days is indicated, the residue measured at maturity was taken for evaluation, as treatment was made before or at planting, and the potatoes are harvested when they are ready. In trials in which the time of maturity of the potatoes was not indicated, the residue level measured at the shortest PHI was used for evaluation.

Trials were reported from the USA and Canada. Twenty-one trials on potatoes were conducted in the USA and twenty-five in Canada. A phorate granulate formulation was applied in-furrow or in a band at planting, at a rate of 2.19 to 266 kg ai/ha. For the post-emergence trials, application was as a band or side dressing at hilling, at the rate of 2.7 to 10 kg ai/ha.

Seven of the USA trials could be evaluated against USA GAP (1.9-4.0 kg ai/ha, PHI 90 days). Total phorate-related residues were < 0.05 (6), 0.08 mg/kg.

Twenty of the Canadian trials could be evaluated against Canadian GAP (2.3–4.3 kg ai/ha, PHI 90 days), yielding total phorate-related residues of < 0.05 (12), 0.07 (2), 0.10, 0.11, 0.12, 0.15, 0.16, 0.27 mg/kg.

The Meeting decided to combine the USA and Canadian trials, yielding the following data set: < 0.05 (18), 0.07 (2), 0.08, 0.10, 0.11, 0.12, 0.15, 0.16, 0.27 mg/kg.

The Meeting agreed to withdraw the previous maximum residue level recommendation for potato (0.2 mg/kg), to be replaced by a recommendation of 0.5 mg/kg. The Meeting estimated an STMR of 0.05, and a HR of 0.27 mg/kg for phorate on potato.

Sugar beet

A total of 16 trials on sugar beets were conducted in the USA in 1985. Ten of these trials were carried out with a single at planting or post-emergence treatment. In the remaining trials two applications, one at planting and the other post-emergence were made. Rates ranged from 1.68 to 3.36 kg ai/ha per application.

Two trials were according to GAP of the USA (1.1-1.7 kg ai/ha, PHI 30 days), yielding total phorate-related residues of < 0.05(2) mg/kg eq. In two trials which received double (2×) rates total residues found were of < 0.05, 0.06 mg/kg eq. Three trials in which a second application was made yielded total residues of < 0.05 (2) and 0.06 mg/kg eq. In three trials in which a 2× at planting application rate was combined with a second application, total residues found were < 0.05 (2), 0.06 mg/kg eq.

Based on the above, the Meeting decided to confirm the present recommendation of 0.05* mg/kg, and estimated an STMR and an HR of 0.05 mg/kg.

Cereal grains

Maize

Forty-five trials on maize (field corn) were reported from the USA. A phorate granular formulation was either applied as a single application in a band at planting or as a double application: one in a band at planting followed by either a side dress beside each row or a foliar treatment at cultivation. Rates per application ranged from 1.12 to 8.8 kg ai/ha.

None of the trials were according to the GAP of the USA (1.1-1.5 kg ai/ha, PHI 30 days). In the trials application rates were exaggerated (2× or 3×) and/or the PHI was unacceptably long. However, in 14 maize trials where phorate was applied twice, at an application rate at GAP or two times GAP and the residue was measured at a PHI of 29 or 30 days, the total phorate-related residue was < 0.01(2), < 0.02 (12) mg/kg. From the application of even more exaggerated rates, finite residues were detected.

Based on the above, the Meeting decided to confirm the present recommendation of 0.05* mg/kg, and estimated a STMR of 0.02 mg/kg for maize.

Sorghum

Eighteen trials on sorghum were reported from the USA. Treatments ranged from one application of a granulate phorate formulation at the rate of 1.22-1.46 kg ai/ha at cultivation or at planting, to 2 applications, one at planting and another at cultivation, at rates of 1.12 up to 7.3 kg ai/ha.

In all but four of the trials, total phorate-related residues (oxidizable to phoratoxon sulfone) were determined by GC-FPD, following Method M-1722. This method is considered inaccurate for sorghum grain because of high recoveries at 0.01 mg/kg eq (> 120%) and high RSD_r (> 20%) at concentrations between 0.1–1.0 mg/kg eq. However, as all results were < 0.05 mg/kg eq, the Meeting decided to include them.

None of the trials were according to GAP of the USA (1.1–1.5 kg ai/ha, PHI 30 days). In the trials application rates were exaggerated (2×) and/or the PHI was unacceptably long. However, in eight trials where the residue was measured at a PHI of 30 days, the total phorate-related residues found were < 0.05 mg/kg eq.

Based on the above, the Meeting decided to confirm the present recommendation of 0.05* mg/kg, and estimated an STMR of 0.05 mg/kg for sorghum grain.

Cotton seed

Fourteen trials on cotton were reported from the USA. The majority of trials were conducted using two application timings. Rates applied ranged from 0.84 to 7.17 kg ai/ha for the first application to 2.47 to 9.86 kg ai/ha for the second.

None of the trials were according to the GAP of the USA ((0.61-2.4 kg ai/ha, PHI 60 days). In the trials application rates were exaggerated (2×) and/or the PHI was unacceptably long. However, in nine trials where the residue was measured at a PHI of 61–65 days, the total phorate-related residue was < 0.05 mg/kg. Two of these trials were at highly exaggerated rates (first application 7.17 kg ai/ha, second application 9.86 kg ai/ha).

Based on the above, the Meeting decided to confirm the present recommendation of 0.05* mg/kg, and estimated an STMR of 0 mg/kg for cotton seed.

Seed for beverages and sweets

Coffee beans

A total of 19 trials on coffee were conducted, two in Colombia, 13 in Brazil, and four in Puerto Rico. Dry unroasted coffee beans were analysed. There was no Colombian or Puerto Rican GAP; Brazilian GAP was 3.0–3.8 g ai/plants for up to 1660 plants /ha, and 5.0–6.2 kg ai/ha for > 1660 plants/ha, with a PHI of 90 days. Trials were considered at GAP when either the application rate in g ai/plant or in kg ai/ha was observed.

Two Colombian trials and two Puerto Rican trials were according to Brazilian GAP, yielding total phorate-related residues of < 0.05 (4) mg/kg eq. All other trials had much higher PHIs and had treatment rates either below or above the GAP rates.

Based on the above and additional information from the remaining trials, the Meeting estimated a maximum residue level of 0.05* mg/kg, and an STMR of 0.05 mg/kg for coffee beans.

Straw, fodder and forage of cereal grains and grasses

Maize forage

For the purpose of estimating the animal dietary burden, the Meeting decided to review data on sweet corn forage coupled with data on maize forage. In all of the nine sweet corn trials and six of the forty-five maize trials residues were measured in green plant material (forage). Rates per application ranged from 1.2 to 8.8 kg ai/ha.

None of the trials were according to GAP of the USA (1.1–1.5 kg ai/ha, waiting period 30 days). In the maize trials residues were measured at PHIs ranging from 83–103 days. In the trials the sweet corn was treated twice at exaggerated rates and/or a PHI that was unacceptably long. Residues were detected at varying levels. The Meeting decided to use data from the trials where two applications were made at 1.46 kg ai/ha, with a PHI of 28–37 days. Total phorate-related residues found were < 0.06, 0.09, and 0.10 mg/kg (wet weight basis).

The Meeting estimated a highest residue of 0.10 mg/kg (wet weight basis) and a median residue of 0.09 mg/kg (wet weight basis) for maize forage.

The Meeting considered that maize forage is not a traded commodity and that the data was insufficient to estimate a maximum residue level. The Meeting decided to withdraw the current recommendation of 0.2 mg/kg.

Maize fodder

In twenty-four of the forty-five trials conducted on maize (field corn) from the USA, residues were measured in dry maize plants (fodder). Rates per application ranged from 1.12 to 8.8 kg ai/ha.

None of the trials were according to the USA GAP (1.1–1.5 kg ai/ha, grazing waiting period 30 days). In the trials the maize was treated twice at rates and above GAP and/or with extended waiting periods. Residues were detected at varying levels. The Meeting decided to use data from trials that were treated twice at rates of 1.12–1.46 kg ai/ha, with a PHI of 29 days. Total phorate-related residues were 0.09 (2), 0.16 and 0.22 mg/kg (wet weight basis).

For the purpose of estimating the animal dietary burden, the Meeting estimated a highest residue of 0.22 mg/kg (wet weight basis) and a median residue of 0.125 mg/kg (wet weight basis) for maize fodder.

The Meeting considered that the data was insufficient to estimate a maximum residue level and decided to withdraw the current recommendation of 0.2 mg/kg.

Sorghum forage (green)

In three of the eighteen reported sorghum trials previously reported, residues were measured in the sorghum forage.

None of the trials were according to USA GAP (1.1–1.5 kg ai/ha, PHI 30 days) as the PHI was too long (47–78 days). The Meeting therefore decided that there were insufficient data from which to derive a conclusion on residue levels in sorghum forage.

Sorghum straw and fodder, dry

In 12 of the 18 trials conducted on sorghum, residues were measured in dry sorghum fodder.

None of the trials were according to USA GAP (1.1-1.5 kg ai/ha, PHI 30 days). In the trials the crop was treated twice at rates above GAP and/or with unacceptably long PHIs. However, in eight trials where the residue was measured at a PHI of 30 days, the total phorate-related residue was < 0.05 mg/kg eq. In these trials, total phorate-related residues (oxidizable to phoratoxon sulfone) were determined by GC-FPD, following Method M-1722. This method is considered inaccurate for sorghum dry fodder because of low recoveries below 0.2 mg/kg eq (< 70%).

Based on the above, the Meeting decided not to estimate an MRL, a highest residue or a median residue for sorghum dry fodder.

Miscellaneous Fodder and Forage crops (group 052)

Cotton fodder, dry

In nine out of the fourteen trials conducted on cotton from the USA, residues were measured in cotton fodder, dry. Most trials consisted of two treatments at rates ranging from 0.84 to 7.17 kg ai/ha for the first application and 2.47 to 9.86 kg ai/ha for the second.

None of the trials were according to USA GAP (0.61–2.4 kg ai/ha, PHI 60 days). In the trials the crop was treated twice at rates above GAP and/or with unacceptably long PHIs. In two trials where the first application was made at a rate of 1.79 kg ai/ha and the second at 2.47 kg ai/ha, with the PHI of 64 or 65 days, residues found were < 0.05 and 0.16 mg/kg.

The Meeting considered that the data was insufficient to estimate a maximum residue level, a highest residue and a median residue for cotton fodder, dry.

Sugar beet tops

In all of the 16 trials on sugar beets conducted in the USA in 1985 residues were measured in sugar beet tops. Ten of these trials were carried out with one treatment either at planting or post-emergence. The rest of the trials consisted of two applications, one at planting and the other post-emergence. Rates ranged from 1.68 to 3.36 kg ai/ha per application.

Four of the trials (study reports PA-724-025 and PA-724-026) were considered not to be acceptable for evaluation because of unacceptably high matrix interferences for sugar beet tops (up to 0.09 mg/kg eq in PA-724-025 and up to 0.41 mg/kg eq in PA-724-026). Only one of the remaining trials was according to USA GAP (1.1–1.7 kg ai/ha, PHI 30 days), yielding total phorate-related residues of < 0.08 mg/kg eq.

The Meeting considered that the data was insufficient to estimate a maximum residue level for sugar beet leaves and tops and decided to withdraw the current recommendation of 1 mg/kg. A highest residue and a median residue also could not be estimated.

Fate of residues in storage and during processing

The Meeting received information on the fate of residues during storage of field treated potatoes at ambient temperatures. Residues declined rapidly, after 23 days in storage it was found that only 33% of the original residue level remained.

The Meeting also received information on the fate of incurred residues of phorate during the processing of potatoes, maize and coffee beans.

Five processing studies were undertaken in which field treated potatoes were either processed into flakes, chips and granules, or were washed, peeled, boiled, baked or fried. In two of those studies, processing factors for potato chips, flakes and granules could not be estimated because residues in the raw agricultural commodity were less than the LOQ. One study was disregarded because residues in the washed potatoes were higher than in the raw agricultural commodity.

Calculated processing factors were < 0.07, < 0.3 for chips, 1.6 for flakes, 1.2, 3.6 for granules, 0.32, 0.49 for washing, 0.25, 0.28 for peeling, 0.13 for boiled with peel, 0.11 for boiled without peel, 0.14 for boiled peel, 0.28 for baked with peel, 0.27 for baked without peel, 2.4 for baked peel, 0.38 for French fries, 0.52, 0.63, 0.73, 0.87 for raw peel, 2.2 for dry peel, 0.36 for microwaved with peel.

In two studies field treated maize was processed into flour and oil. One study was disregarded because residues in the raw agricultural commodity (0.036 mg/kg) were lower than the LOQ (0.05 mg/kg). Calculated processing factors were 12 for hulls, 2.3 for germ, < 0.81 for grits, 2.7 for meal, 2.3 for flour, 4.0 for crude oil, expeller, 1.0 for presscake, expeller, 4.7 for crude oil, solvent extracted, < 0.81 for presscake, solvent extracted, 5.8 for refined oil, < 0.81 for soapstock, and < 0.81 for deodorized oil.

Green coffee beans were sprayed with a phorate sulfone solution in acetone at a final concentration of 0.1 or 4.6 mg/kg. Beans were roasted at 260°C for 5 to 6 minutes in an oven, cooled and ground. Residues in the roasted beans were < 0.05 mg/kg. Because processing was not carried out with incurred residues, no processing factors were calculated.

Field treated green coffee beans were harvested from plots treated at an exaggerated rate. Harvested coffee beans were air dried for a period of 21 days. Green beans were roasted at 260°C for 5 to 6 minutes. The calculated processing factor for roasted beans was 0.067.

In the table below, relevant processing factors for potato, maize and coffee commodities are summarized. Using the HRs for potato, maize and coffee bean (0.27, 0.02 and 0.05mg/kg, respectively) the Meeting estimated HR-Ps for their processed commodities as listed below. Furthermore, using the STMRs for potato, maize and coffee bean (0.05, 0.02, and 0.05 mg/kg) the Meeting estimated STMR-Ps for these commodities.

Table 64. Calculated processing factors.

Commodity	Processing factors	Processing factor (median or best estimate)	STMR-P	HR-P
Washed potatoes	0.32, 0.49	0.405	0.02025	0.10935
Peeled potatoes	0.25, 0.28	0.265	0.01325	0.07155
Potatoes boiled with peel	0.13		0.0065	0.0351

Potatoes boiled without peel	0.11		0.0055	0.0287
Boiled potato peels	0.14		0.007	0.0378
Potatoes baked with peel	0.28		0.014	0.0756
Potatoes baked without peel	0.27		0.0135	0.0729
Baked potato peels	2.4		0.12	0.648
French fries	0.38		0.019	0.1026
Raw potato peels	0.52, 0.63, 0.73, 0.87	0.68	0.034	0.1836
Dry potato peels	2.2		0.11	0.594
Potatoes microwaved with peel	0.36		0.018	0.0972
Maize flour	2.3		0.046	0.046
Maize crude oil, expeller	4.0		0.08	0.08
Maize crude oil, solvent extracted	4.7		0.094	0.094
Maize deodorized oil#	< 0.81		0.0162	0.0162
Roasted coffee beans	0.067		0.00335	0.00335

taken to be edible oil

Using the highest residue for maize (0.02 mg/kg) and the processing factors as indicated above, the Meeting estimated a maximum residue level of 0.05 mg/kg in maize flour, and 0.1 mg/kg in maize oil, crude, and 0.02 mg/kg in maize oil, edible. For the remaining commodities no maximum residue levels were estimated, either because the commodity is not in the Codex system or because the MRL would be lower than that of the raw agricultural commodity.

The Meeting considered the appropriate HR-P and STMR-P to be used in the dietary intake calculation for potatoes. It was recognized that raw potatoes are not consumed, but that potatoes are not always eaten peeled. The percentage of people who eat unpeeled potatoes however is unknown. Also the ratio of boiled/baked/microwaved/fried for potatoes is unknown. The Meeting therefore decided to use the HR-P and STMR-P on potatoes, microwaved with peel in the dietary intake calculations for potatoes since this represents the worst-case situation.

Farm animal dietary burden

The Meeting estimated the dietary burden of phorate residues in farm animals from the diets listed in Appendix IX of the *FAO Manual* (FAO, 2002). One feed commodity only from each Codex Commodity Group was used. Calculation from the HR values provides the concentrations in feed suitable for estimating MRLs for animal commodities, while calculation from the STMR values for feed is suitable for estimating STMR values for animal commodities. In the case of processed commodities, the STMR-P value is used for both intake calculations.

Table 65. Estimated maximum dietary burden of farm animals.

Commodity	Group	Residue mg/kg	Basis	% Dry matter	Residue, on dry wt mg/kg	*Diet content (%)*			Residue contribution, mg/kg		
						Beef cattle	*Dairy cows*	*Poultry*	Beef cattle	Dairy cows	Poultry
Cottonseed	SO	0	highest residue	88%	0	*25%*	*10%*	*NU*§			
Maize grain	GC	0.02	highest residue	88%	0.023	*80%*	*40%*	*80%*			
Maize forage	AF	0.10	highest residue	40%	0.25	*40%*	***50%***	*NU*		0.125	
Maize fodder	AS	0.22	highest residue	83%	0.26	***25%***	*15%*	*NU*	0.065		
Potato culls	VR	0.27	HR	20%	1.35	***75%***	***40%***	*NU*	1.0125	0.54	
Potato processed waste#	AB	0.1836	HR-P	15%	1.22	*5%*	*10%*	*NU*			
Sorghum grain	GC	0.05	highest residue	86%	0.058	*20%*	*40%* ***(10%)***	***80%***		0.0058	0.0464

Soybean seeds	VD	0	highest residue	89%	0	*15%*	*15%*	*20%*			
						Maximum dietary burden			**1.08**	**0.67**	**0.05**

take data raw potato peel; § NU – Not Used

Table 66. Estimated median dietary burden of farm animals.

Commodity	Group	Residue mg/kg	Basis	% Dry matter	Residue, on dry wt mg/kg	*Diet content (%)*			Residue contribution, mg/kg		
						Beef cattle	*Dairy cows*	*Poultry*	Beef cattle	Dairy cows	Poultry
Cottonseed	SO	0	STMR	88%	0	*25%*	*10%*	*NU*§			
Maize grain	GC	0.02	STMR	88%	0.023	*80%*	*40%*	*80%*			
Maize forage	AF	0.09	median residue	40%	0.225	*40%*	***50%***	*NU*		0.1125	
Maize fodder	AS	0.125	Median residue	83%	0.151	***25%***	*15%*	*NU*	0.0378		
Potato culls	VR	0.05	STMR	20%	0.25	***75%***	***40%***	*NU*	0.1875	0.1	
Potato processed waste#	AB	0.034	STMR	15%	0.227	*5%*	*10%*	*NU*			
Sorghum grain	GC	0.05	STMR	86%	0.058	*20%*	*40%* ***(10%)***	***80%***		0.0058	0.0464
Soybean seeds	VD	0	STMR	89%	0	*15%*	*15%*	*20%*			
						Median dietary burden			**0.22**	**0.22**	**0.05**

take data raw potato peel; § NU – Not Used

Farm animal feeding studies

The Meeting received information on feeding studies for calves, lactating cows and laying hens.

Two groups of three Holstein calves were dosed at levels of 0 and 0.1 mg ai/kg bw for 14 consecutive days by gelatin capsules. The calves weighed 220-234 kg (average 227 kg). Dosage as ppm in the feed was not stated. Assuming a daily feed intake of 4% of the bodyweight, the dose would be 2.5 ppm. Total phorate-related residues (oxidizable to phoratoxon sulfone) in thigh muscle, fat, liver and kidney were all below the LOQ of 0.1 mg/kg. At a dose equivalent to 0.1 mg ai/kg bw, animals showed no significant differences in red blood cell cholinesterase activity as compared to controls. When levels were increased to 0.2 mg ai/kg bw, animals showed significant depression of red blood cell cholinesterase activity.

Three groups of three lactating Holstein cows were dosed twice daily via gelatin capsules at levels of 0, 0.05, and 0.1 mg ai/kg bw per day for 14 consecutive days. The cows weighed 485–505 kg (average 493 kg). Dosage as ppm in the feed was not stated. Assuming a daily feed intake of 4% of the bodyweight, the doses would be 1.25 and 2.5 ppm. Milk was sampled daily and a.m. and p.m. milkings were pooled. Tissues were not collected. Total phorate-related residues (oxidizable to phoratoxon sulfone) were determined by their cholinesterase inhibitive power in an electrometric cholinesterase assay, method B, which is an unspecific method. Total phorate-related residues (oxidizable to phoratoxon sulfone) in milk from the 0.05 mg ai/kg dose rate were all below the LOQ of 0.02 mg/kg eq. In samples from the 0.1 mg ai/kg bw dose group residues were found from day 7 onwards ranging from 0.03–0.06 mg/kg.

Fourteen non-pregnant lactating Holstein cows were divided into three treatment groups. Animals in groups A (4 cows), B (4 cows), and C (6 cows) were dosed orally once a day for 28 consecutive days with gelatine capsules using a balling gun. For two cows of group C, a withdrawal period of up to 14 days was included. Using an average actual daily feed intake of 20 kg dry matter/day, mean actual doses were calculated to be equivalent 0, 1.39 and 3.21 ppm. Milk samples were collected each day and p.m. and a.m. milkings were pooled. Animals were sacrificed within 20 hrs after the last dose and samples of loin muscle, omental fat, both kidneys and whole liver were collected. In cows from all dose groups total phorate-related residues (oxidizable to phoratoxon sulfone) were below the LOQ of < 0.005 mg/kg for whole milk (day 2 to day 28) or < 0.02 mg/kg for tissues.

In a preliminary dose-finding study, animals showed severe signs of organophosphate poisoning (diarrhoea, stiffness, muscular tremors) at doses equivalent to 14 ppm, and mild signs of organophosphate poisoning (depression, salivation, off feed consumption) at doses equivalent to 7 and 5 ppm. At doses equivalent to 1.39 and 3.21 ppm, as used in the final study, animals showed no signs of organophosphate poisoning.

Four groups of six laying hens were dosed at levels of 0, 0.1, 0.3 and 1.0 ppm as total phorate (1:1 phorate: phoratoxon sulfone) for 21 consecutive days. A composite egg sample from each group was collected only on the final day of treatment. The hens were sacrificed 2 to 3 h after final dosing with muscle, fat, liver and kidney samples collected. Total phorate-related residues (oxidizable to phoratoxon sulfone) in muscle, liver and kidney and eggs were all below the LOQ of 0.05 mg/kg and below the LOQ of 0.06 mg/kg in fat.

Residues in animal commodities

In the most recent feeding study where lactating cows were dosed at 1.39 and 3.21 mg ai/kg dry feed, no total phorate-related residues were detected in tissues and milk. Therefore no residues are to be expected at the maximum calculated dietary burden of 1.08 mg/kg feed for beef cattle and 0.67 mg/kg for dairy cattle.

In the feeding study where laying hens were dosed at 0.1, 0.3 and 1.0 mg/kg feed, no total phorate-related residues were detected in tissues and eggs. Therefore no residues are to be expected at the maximum calculated dietary burden of 0.05 mg/kg feed for poultry.

The Meeting estimated a maximum residue level of 0.02* mg/kg in mammalian meat and offal and HRs and STMRs of 0.02 mg/kg. For milk, the Meeting estimated a maximum residue level of 0.01* mg/kg and an STMR of 0.005 mg/kg.

The Meeting estimated a maximum residue level of 0.05* mg/kg in poultry meat and eggs and HRs and STMRs of 0 mg/kg.

RECOMMENDATIONS

On the basis of the data from supervised trials the Meeting concluded that the residue levels listed below are suitable for establishing maximum residue limits and for IEDI and IESTI assessment.

Definition of the residue for compliance with MRL and for estimation of dietary intake, both for animal and plant commodities:

Sum of parent, its oxygen analogue, and their sulphoxides and sulphones, expressed as phorate.

Table 67. Summary of recommendations.

COMMODITY		RECOMMENDED MRL, mg/kg		STMR or STMR-P mg/kg	HR or HR-P, mg/kg
CCN	Name	New	Previous		
VD 0071	Beans (dry)	0.05*	-	0.05	-
SB 0716	Coffee beans	0.05*	-	0.05	-
VP 0526	Common bean (pods and/or immature seeds)	0.05*	0.1	0.05	0.05

SO 0691	Cotton seed	0.05*	0.05	0	-
MO 0105	Edible offal (mammalian)	0.02*	-	Liver 0.02 kidney 0.02	Liver 0.02 kidney 0.02
PE 0112	Eggs	0.05*	0.05*	0	0
AM 1051	Fodder beet	W	0.05		
GC 0645	Maize	0.05*	0.05	0.02	-
CF 1255	Maize flour	0.05	-	0.046	-
AS 0645	Maize fodder	W	0.2 fresh wt		
AF 0645	Maize forage	W	0.2 fresh wt		
OC 0645	Maize oil, crude	0.1	-	0.069	-
OR 0645	Maize oil, edible	0.02	-	0.0162	-
MM 0095	Meat (from mammals other than marine mammals)	0.02*	0.05*	Muscle 0.02 Fat 0.02	Muscle 0.02 Fat 0.02
ML 0106	Milks	0.01*	0.05*	0.005	
SO 0697	Peanut	W	0.1		
OC 0697	Peanut oil, Crude	W	0.05*		
OR 0697	Peanut oil, Edible	W	0.05*		
VR 0589	Potato	0.5	0.2	0.05	0.27
	Potatoes, microwaved with peel			0.018	0.0972
PM 0110	Poultry meat	0.05*	-	Muscle 0 Fat 0	Muscle 0 Fat 0
GC 0651	Sorghum	0.05*	0.05	0.05	-
VD 0541	Soya bean (dry)	0.05*	0.05	0	-
VR 0596	Sugar beet	0.05*	0.05	0.05	0.05
AV 0596	Sugar beet leaves or tops	W	1		
VO 0447	Sweet corn (corn-on-the-cob)	W	0.05		
GC 0654	Wheat	W	0.05		

DIETARY RISK ASSESSMENT

Long-term intake

The International Estimated Daily Intakes (IEDI) of phorate, based on the STMRs estimated for 18 commodities, for the five GEMS/Food regional diets, were in the range of 9 to 20% of the maximum ADI (0.0007 mg/kg bw), see Annex 3 of 2005 JMPR Report. The Meeting concluded that the long-term intake of residues of phorate resulting from its uses that have been considered by JMPR are unlikely to present a public health concern.

Short-term intake

The International Estimated Short Term Intake (IESTI) for phorate was calculated for 18 food commodities for which maximum residue levels were estimated and for which consumption data was available. The results are shown in Annex 4 of the 2005 JMPR Report.

The IESTI represented 0–50% of the ARfD (0.003 mg/kg bw) for the general population and 0–120% of the ARfD for children. The value of 120% represents the IESTI for potato, microwaved with peel. The Meeting concluded that the short-term intake of residues of phorate, resulting from its uses other than on potato that have been considered by the JMPR, is unlikely to present a public health concern. The information provided to the Meeting precludes an estimate that the acute dietary intake from the consumption of potatoes by children aged 6 years and under would be below the ARfD.

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PA-790-019	Bohn WR and Rose R	1979	THIMET phorate (CL 35,024/10-G): residues of total CL 35,024-related compounds in coffee beans (Brazil, 1978). Princeton, NJ, USA: American Cyanamid Company Inc., report C-1637. Cyanamid code PA-790-019, BASF code V614. Non-GLP. Unpublished.
PA-790-017	Bohn WR and Rose R	1979	THIMET phorate (CL 35,024/10-G): residues of total CL 35,024-related compounds in coffee beans (Puerto Rico, 1978). Princeton, NJ, USA: American Cyanamid Company Inc., report C-1633. Cyanamid code PA-790-017, BASF code V612. Non-GLP. Unpublished.
PA-790-018	Bohn WR and Rose R	1979	THIMET phorate (CL 35,024/10-G): residues of total CL 35,024-related compounds in coffee beans (Puerto Rico, 1978). Princeton, NJ, USA: American Cyanamid Company Inc., report C-1634. Cyanamid code PA-790-018, BASF code V613. Non-GLP. Unpublished.
PA-905-046	Bowman JS and Casida JE	1957	Metabolism of the systemic insecticide O,O-diethyl S-ethylthiomethyl phosphorodithioate (Thimet) in plants. J. Agric. Food Chem. 5(3):192-197. Cyanamid code PA-905-046. BASF code V685. Non-GLP. Published.
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PA-640-003	Brindle PA	1992	CL 35,024: confined accumulation study of carbon-14 labelled CL 35,024 using barley, carrots, lettuce and peas as rotational crops. Princeton, NJ, USA: American Cyanamid Company, report PD-M 29-42, project ID: M90P024CA2. Cyanamid code PA-640-003. BASF code V378. GLP. Unpublished.
PA-640-004	Brindle PA	1994	CL 35,024: Confined accumulation study of carbon-14 labelled CL 35,024

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PA-640-001	Chiu T	1987	THIMET insecticide, phorate (CL 35,024): confined accumulation studies in corn, lettuce, radish, table beet as rotational crops. Princeton, NJ, USA: American Cyanamid Company, report PD-M 24-31. Cyanamid code PA-640-001. BASF code V376. Non-GLP. Unpublished.
PA-640-002	Chiu T	1988	Phorate (CL 35,204): confined accumulation study in spring wheat as a rotational crop. Princeton, NJ, USA: American Cyanamid Company, report PD-M 25-45. Cyanamid code PA-640-002. BASF code V377. Non-GLP. Unpublished.
PA-724-014	Devine JM and Green A	1990	CL 35,024 (Phorate/20-G): residues of total CL 35,024-related compounds in potato tubers and processed potato fractions (potato chips, flakes, and granules). Princeton, NJ, USA: American Cyanamid Company Inc., report C-3291. Cyanamid code PA-724-014. BASF code V458. Non-GLP. Unpublished.
PA-724-012	Dixon C and Gorrell M	1990	CL 35,024 (phorate/20G): residues of total CL 35,024-related residues in potatoes. Princeton, NJ, USA: American Cyanamid Company Inc., report C-3426. Cyanamid code PA-724-012. BASF code V456. Non-GLP. Unpublished.
PA-724-016	Dixon C and Gorrell M	1990	CL 35,024 (phorate/20G): residues of total CL 35,024-related residues in potatoes. Princeton, NJ, USA: American Cyanamid Company Inc., report C-3471. Cyanamid code PA-724-016. BASF code V460. Non-GLP. Unpublished.
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PA-790-014	Elenewski C and Whitney K	1978	THIMET LC-8 and 10-G (CL 35,024): determination of THIMET-related residues in unroasted coffee beans (Cafelandia, Brazil, 1976-77). Princeton, NJ, USA: American Cyanamid Company Inc., report C-1338. Cyanamid code PA-790-014, BASF code V609. Non-GLP. Unpublished.
PA-790-015	Elenewski C and Whitney K	1978	THIMET LC-8 (CL 35,024): determination of THIMET-related residues in unroasted coffee beans (Guaranta, Brazil, 1976-77). Princeton, NJ, USA: American Cyanamid Company Inc., report C-1339. Cyanamid code PA-790-015, BASF code V610. Non-GLP. Unpublished.
PA-790-016	Elenewski C and Whitney K	1978	THIMET 10-G (CL 35,024): determination of phorate-related residues in unroasted coffee beans (Jau, Brazil, 1976-77). Princeton, NJ, USA: American Cyanamid Company Inc., report C-1340. Cyanamid code PA-790-016, BASF code V611. Non-GLP. Unpublished.
PA-905-044	Fuhremann TW & Lichtenstein EP	1980	A comparative study of the persistence, movement, and metabolism of six carbon-14 insecticides in soils and plants. USA: University of Wisconsin. J. Agric. Food Chem. 28:446-452. Cyanamid code PA-905-044. BASF code V683. Non-GLP. Unpublished.
PA-244-034	Gross JR	1990	Phorate (CL 35,024): characteristics of phorate (CL 35,024) and its phosphorylated metabolites through FDA multiresidue methods. Princeton, NJ, USA: American Cyanamid Company Inc., report C-3378. Cyanamid code PA-244-034. BASF code V067. GLP. Unpublished.
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PA-705-001	Higham JW	1969	Total THIMET® residues in chicken tissues (muscle, fat, liver, kidney and eggs). Princeton, NJ, USA: American Cyanamid Company Inc., report no C-205. Cyanamid code PA-705-001. BASF code V387. Non-GLP. Unpublished.
PA-731-010	Higham JW	1981	THIMET phorate (CL 35,024/15-G): residues of total CL 35,024-related compounds in field corn silage, fodder and grain (BOTR; NE, 1981. Princeton, NJ, USA: American Cyanamid Company Inc., report C-1980. Cyanamid code PA-731-010. BASF code V576. Non-GLP. Unpublished.
PA-244-033	Higham JW	1986	THIMET phorate (CL 35,024): validation of GC method M-1618 for the determination of total CL 35,024-related residues in corn commodities (field corn grain, sweet corn kernels plus cob, and green and dry corn plants). Princeton, NJ, American Cyanamid Company Inc., report C-2682. Cyanamid code PA-244-033. BASF code V066. Non-GLP. Unpublished.
PA-244-028	Higham JW	1986	THIMET phorate (CL 35,024): validation of GC method M 1653 for the determination of total CL 35,024-related residues in green soybean plant, hay and seed. USA: Analytical Bio-Chemistry Laboratories, report C-2791. Cyanamid code PA-244-028. BASF code V061. Non-GLP. Unpublished.
PA-723-002	Higham JW	1986	THIMET (phorate, CL 35,024/20-G): residues of total CL 35,024-related

			compounds in sweet corn plants and kernels plus cob (BAND, CULT; WI, 1985). USA: Hazleton Laboratories America Inc., report C-2732. Cyanamid code PA-723-002. BASF code V433. Non-GLP. Unpublished.
PA-723-003	Higham JW	1986	THIMET (phorate, CL 35,024/20-G): residues of total CL 35,024-related compounds in sweet corn plants and kernels plus cob (BAND, FL, 1985). USA: Hazleton Laboratories America Inc., report C-2738. Cyanamid code PA-723-003. BASF code V434. Non-GLP. Unpublished.
PA-723-004	Higham JW	1986	THIMET (phorate, CL 35,024/20-G): residues of total CL 35,024-related compounds in sweet corn plants and kernels plus cob and plant (BAND, CULT, FL, 1985). USA: Hazleton Laboratories America Inc., report C-2739. Cyanamid code PA-723-004. BASF code V435. Non-GLP. Unpublished.
PA-723-007	Higham JW	1986	THIMET (phorate, CL 35,024/20-G): residues of total CL 35,024-related compounds in sweet corn plants and kernels plus cob (BAND, CULT; OR, 1985). USA: Hazleton Laboratories America Inc., report C-2730. Cyanamid code PA-723-007. BASF code V438. Non-GLP. Unpublished.
PA-730-051	Higham JW	1986	THIMET (phorate, CL 35,024/20-G): residues of total CL 35,024-related compounds in field corn grain (BAND, CULT; OH, 1985). USA: Hazleton Laboratories America Inc., report C-2733. Cyanamid code PA-730-051. BASF code V539. Non-GLP. Unpublished.
PA-730-066	Higham JW	1986	THIMET (phorate, CL 35,024/20-G): residues of total CL 35,024-related compounds in field corn grain (BAND, CULT, FOL; NE, 1985). USA: Hazleton Laboratories America Inc., report C-2687. Cyanamid code PA-730-066. BASF code V554. Non-GLP. Unpublished.
PA-730-055	Higham JW	1986	THIMET (phorate, CL 35,024/20-G): residues of total CL 35,024-related compounds in field corn plant and grain (BAND, CULT, FOL; NE, 1985). USA: Hazleton Laboratories America Inc., report C-2688. Cyanamid code PA-730-055. BASF code V543. Non-GLP. Unpublished.
PA-730-056	Higham JW	1986	THIMET (phorate, CL 35,024/20-G): residues of total CL 35,024-related compounds in field corn plant and grain (BAND, CULT, FOL; NE, 1985). USA: Hazleton Laboratories America Inc., report C-2689. Cyanamid code PA-730-056. BASF code V544. Non-GLP. Unpublished.
PA-730-057	Higham JW	1986	THIMET (phorate, CL 35,024/20-G): residues of total CL 35,024-related compounds in field corn (BAND, FOL; OH, 1985). USA: Hazleton Laboratories America Inc., report C-2694. Cyanamid code PA-730-057. BASF code V545. Non-GLP. Unpublished.
PA-730-058	Higham JW	1986	THIMET (phorate, CL 35,024/20-G): residues of total CL 35,024-related compounds in field corn (BAND, CULT; IL, 1985). USA: Hazleton Laboratories America Inc., report C-2698. Cyanamid code PA-730-058. BASF code V546. Non-GLP. Unpublished.
PA-730-060	Higham JW	1986	THIMET (phorate, CL 35,024/20-G): residues of total CL 35,024-related compounds in field corn (BAND, FOL; IL, 1985). USA: Hazleton Laboratories America Inc., report C-2700. Cyanamid code PA-730-060. BASF code V548. Non-GLP. Unpublished.
PA-730-052	Higham JW	1986	THIMET (phorate, CL 35,024/20-G): residues of total CL 35,024-related compounds in field corn grain (BAND, CULT; OH, 1985). USA: Hazleton Laboratories America Inc., report C-2737. Cyanamid code PA-730-052. BASF code V540. Non-GLP. Unpublished.
PA-730-053	Higham JW	1986	THIMET (phorate, CL 35,024/20-G): residues of total CL 35,024-related compounds in field corn grain (BAND, CULT; FOL, MN, 1985). USA: Hazleton Laboratories America Inc., report C-2740. Cyanamid code PA-730-053. BASF code V541. Non-GLP. Unpublished.
PA-244-021	Higham JW	1987	THIMET phorate (CL 35,024): validation of GC method M-1700 for the determination of total CL 35,024-related residues in green cotton plant, dry cotton plant and cottonseed. USA: Analytical Bio-Chemistry Laboratories, report C-2855. Cyanamid code PA-244-021. BASF code V054. Non-GLP. Unpublished.
PA-244-018	Higham JW	1987	THIMET phorate (CL 35,024): validation of GC method M-1708 for the determination of total CL 35,024-related residues in sugar beet tops and roots. USA: Analytical Bio-Chemistry Laboratories Inc., report C-2871. Cyanamid code PA-244-018. BASF code V051. Non-GLP. Unpublished.
PA-244-015	Higham JW	1987	THIMET phorate (CL 35,024): validation of GC method M-1718 for the determination of total CL 35,024-related residues in bean plant foliage, bean hay, green beans and dry beans. USA: Hazleton Laboratories America Inc., report C-2881. Cyanamid code PA-244-015. BASF code V048. Non-GLP. Unpublished.
PA-244-016	Higham JW	1987	THIMET phorate (CL 35,024): validation of GC method M-1722 for the determination of total CL 35,024-related residues in sorghum plant (green and

			dry) and grain. USA: Hazleton Laboratories America Inc., report C-2894. Cyanamid code PA-244-016. BASF code V049. Non-GLP. Unpublished.
PA-720-023	Higham JW	1987	THIMET phorate (CL 35,024/20-G): residues of total CL 35,024-related compounds in green bean plant and seeds (BAND, DRILL; OR, 1985). USA: Hazleton Laboratories America Inc., report C-2893. Cyanamid code PA-720-023. BASF code V420. Non-GLP. Unpublished.
PA-720-017	Higham JW	1987	THIMET phorate (CL 35,024/20-G): residues of total CL 35,024-related compounds in green beans and plants (BAND, DRILL; OR, 1985). USA: Hazleton Laboratories America Inc., report C-2884. Cyanamid code PA-720-017. BASF code V414. Non-GLP. Unpublished.
PA-720-018	Higham JW	1987	THIMET phorate (CL 35,024/20-G): residues of total CL 35,024-related compounds in snap bean foliage, hay and seed (BAND, DRILL; MI, 1985). USA: Hazleton Laboratories America Inc., report C-2885. Cyanamid code PA-720-018. BASF code V415. Non-GLP. Unpublished.
PA-720-021	Higham JW	1987	THIMET phorate (CL 35,024/20-G): residues of total CL 35,024-related compounds in snap bean foliage, hay and seed (BAND, DRILL; MI, 1985). USA: Hazleton Laboratories America Inc., report C-2888. Cyanamid code PA-720-021. BASF code V418. Non-GLP. Unpublished.
PA-720-019	Higham JW	1987	THIMET Phorate (CL 35,024/20-G): residue of total CL 35,024-related compounds in dry bean hay, foliage, and seed (BAND, IF; MI, 1985). USA: Hazleton Laboratories America Inc., report C-2886. Cyanamid code PA-720-019. BASF code V416. Non-GLP. Unpublished.
PA-720-022	Higham JW	1987	THIMET Phorate (CL 35,024/20-G): residue of total CL 35,024-related compounds in dry bean plant, hay, and seed (BAND, DRILL; ID, 1985). USA: Hazleton Laboratories America Inc., report C-2892. Cyanamid code PA-720-022. BASF code V419. Non-GLP. Unpublished.
PA-720-009	Higham JW	1987	THIMET Phorate (CL 35,024/20-G): residue of total CL 35,024-related compounds in green soybean plant, hay and seed (BAND, IF; KS, 1985). USA: Analytical Bio-Chemistry Laboratories, report C-2837. Cyanamid code PA-720-009. BASF code V406. Non-GLP. Unpublished.
PA-720-024	Higham JW	1987	THIMET Phorate (CL 35,024/20-G): residue of total CL 35,024-related compounds in green soybean plant, hay and seed (BAND, IF; AR, 1985). USA: Analytical Bio-Chemistry Laboratories, report C-2838. Cyanamid code PA-720-024. BASF code V421. Non-GLP. Unpublished.
PA-720-025	Higham JW	1987	THIMET Phorate (CL 35,024/20-G): residue of total CL 35,024-related compounds in green soybean plants and seed (BAND, DRILL; MN, 1985). USA: Analytical Bio-Chemistry Laboratories, report C-2839. Cyanamid code PA-720-025. BASF code V422. Non-GLP. Unpublished.
PA-720-026	Higham JW	1987	THIMET Phorate (CL 35,024/20-G): residue of total CL 35,024-related compounds in green soybean plant, hay and seed (BAND, IF; MS, 1985). USA: Analytical Bio-Chemistry Laboratories, report C-2840. Cyanamid code PA-720-026. BASF code V423. Non-GLP. Unpublished.
PA-724-020	Higham JW	1987	THIMET Phorate (CL 35,024/20-G): residues of total CL 35,024-related compounds in sugar beet tops and roots (AER, ND, 1985). USA: Analytical Bio-Chemistry Laboratories, report C-2918. Cyanamid code PA-724-020. BASF code V464. Non-GLP. Unpublished.
PA-724-021	Higham JW	1987	THIMET Phorate (CL 35,024/20-G): residues of total CL 35,024-related compounds in sugar beet tops and roots (BAND, IF, FOL, ND, 1985). USA: Analytical Bio-Chemistry Laboratories, report C-2919. Cyanamid code PA-724-021. BASF code V465. Non-GLP. Unpublished.
PA-724-025	Higham JW	1987	THIMET Phorate (CL 35,024/20-G): residues of total CL 35,024-related compounds in sugar beet tops and roots (BAND, POST, CA, 1985). USA: Analytical Bio-Chemistry Laboratories, report C-2873. Cyanamid code PA-724-025. BASF code V469. Non-GLP. Unpublished.
PA-724-026	Higham JW	1987	THIMET Phorate (CL 35,024/20-G): residues of total CL 35,024-related compounds in sugar beet tops and roots (AER, CA, 1985). USA: Analytical Bio-Chemistry Laboratories, report C-2874. Cyanamid code PA-724-026. BASF code V470. Non-GLP. Unpublished.
PA-730-035	Higham JW	1987	THIMET Phorate (CL 35,024/20-G): residues of total CL 35,024-related residues in sorghum plant and grain (BAND + AER; TX, 1985). USA: Hazleton Laboratories Inc, report C-2898. Cyanamid code PA-730-035. BASF code V523. Non-GLP. Unpublished.
PA-730-036	Higham JW	1987	THIMET Phorate (CL 35,024/20-G): residues of total CL 35,024-related residues in sorghum plant and grain (BAND + BROAD; TX, 1985). USA: Hazleton Laboratories Inc, report C-2899. Cyanamid code PA-730-036. BASF code V524. Non-GLP. Unpublished.
PA-730-037	Higham JW	1987	THIMET Phorate (CL 35,024/20-G): residues of total CL 35,024-related

			residues in sorghum plant and grain (BAND + AER; KS, 1985). USA: Hazleton Laboratories Inc, report C-2900. Cyanamid code PA-730-037. BASF code V525. Non-GLP. Unpublished.
PA-730-038	Higham JW	1987	THIMET Phorate (CL 35,024/20-G): residues of total CL 35,024-related residues in sorghum plant and grain (BAND + FOL; TX, 1985). USA: Hazleton Laboratories Inc, report C-2901. Cyanamid code PA-730-038. BASF code V526. Non-GLP. Unpublished.
PA-750-005	Higham JW	1987	THIMET Phorate (CL 35,024/20-G): residues of total CL 35,024-related compounds in cotton plant and seed (IF + SIDE; MS, 1985). Analytical Bio-chemistry Laboratories Inc., report C-2857. Cyanamid code PA-750-005. BASF code V591. Non-GLP. Unpublished.
PA-750-006	Higham JW	1987	THIMET Phorate (CL 35,024/20-G): residues of total CL 35,024-related compounds in cotton plant and seed (IF + SIDE; TX, 1985). Analytical Bio-chemistry Laboratories Inc., report C-2858. Cyanamid code PA-750-006. BASF code V592. Non-GLP. Unpublished.
PA-750-007	Higham JW	1987	THIMET Phorate (CL 35,024/20-G): residues of total CL 35,024-related compounds in cotton plant and seed (IF + SIDE; CA, 1985). Analytical Bio-chemistry Laboratories Inc., report C-2859. Cyanamid code PA-750-007. BASF code V593. Non-GLP. Unpublished.
PA-750-008	Higham JW	1987	THIMET Phorate (CL 35,024/20-G): residues of total CL 35,024-related compounds in cotton plant and seed (IF + SIDE; AL, 1985). Analytical Bio-chemistry Laboratories Inc., report C-2860. Cyanamid code PA-750-008. BASF code V594. Non-GLP. Unpublished.
PA-750-009	Higham JW	1987	THIMET Phorate (CL 35,024/20-G): residues of total CL 35,024-related compounds in cotton plant and seed (IF + SIDE; AZ, 1985). Analytical Bio-chemistry Laboratories Inc., report C-2863. Cyanamid code PA-750-009. BASF code V595. Non-GLP. Unpublished.
PA-244-008	Higham JW	1988	CL 35,024 (phorate): validation of GC method M-1618 for the determination of total CL 35,024-related residues in corn grain and dry corn plants. USA: Analytical Bio-Chemistry Laboratories, report C-3074. Cyanamid code PA-244-008. BASF code V041. Non-GLP. Unpublished.
PA-326-002	Higham JW	1994	Phorate (CL 35,024): twelve-month freezer stability of phorate and related compounds (CL 35,024, CL 18,177, CL 18,161, CL 4,259, CL 18,162, CL 10,061) in dry beans. Princeton, NJ, USA: American Cyanamid Company Inc., report RES 94-044. Cyanamid code PA-326-002. BASF code V102. GLP. Unpublished. **Extended storage stability is found in Higham 1995, PA-326-016.**
PA-326-016	Higham JW	1995	Phorate (CL 35,024): freezer stability of residues of phorate and related compounds (CL 35,024; CL 18,177; CL 18,161; CL 4,259; CL 18, 162; CL 18,061) in dry beans. Princeton, NJ, USA: American Cyanamid Company Inc., report RES 95-114. Cyanamid code PA-326-016. BASF code V116, GLP, Unpublished.
PA-730-031	Higham JW and Fisher RK	1988	CL 35,024 (phorate) and MO 70,616 (esfenvalerate) (15-G): residues of total CL 35,024-related compounds and MO 70,616 in dry field corn plants and grain (BAND; IL, 1986). USA: Analytical Bio-Chemistry Laboratories, report no C-3077. Cyanamid code PA-730-031. BASF code V519. Non-GLP. Unpublished.
PA-730-032	Higham JW and Fisher RK	1988	CL 35,024 (phorate) and MO 70,616 (esfenvalerate) (15-G): residue of total CL 35,024-related compounds and MO 70,616 in dry field corn plants and grain (BAND; NE, 1986). USA: Analytical Bio-Chemistry Laboratories, report no C-3079. Cyanamid code PA-730-032. BASF code V520. Non-GLP. Unpublished.
PA-705-009	Hill R	1961	Thimet phorate residue studies in dairy animals. Berkeley, CA, USA: Diablo Laboratories Inc, report no 2F4036. Cyanamid code PA-705-009. BASF code V395. Non-GLP. Unpublished.
PA-440-003	Hussain MN	1985	Thimet insecticide, phorate (CL 35,024): metabolism of carbon-14 labeled CL 35,024 in lactating goats. Princeton, NJ, USA: American Cyanamid Company, report PD-M Volume 22-30. Cyanamid code PA-440-003. BASF code V184. Non-GLP. Unpublished.
PA-440-004	Hussain MN	1986	Thimet insecticide, phorate (CL 35,024): metabolic fate of carbon-14 labeled CL 35,024 in milk and various tissues of lactating goats. Princeton, NJ, USA: American Cyanamid Company, report PD-M Volume 23-3. Cyanamid code PA-440-004. BASF code V185. Non-GLP. Unpublished. **This report is replaced by report PA-440-005.**
PA-440-005	Hussain MN	1986	Thimet insecticide, phorate (CL 35,024): metabolic fate of carbon-14 labeled CL 35,024 in milk and various tissues of lactating goats. Princeton, NJ, USA: American Cyanamid Company, report PD-M Volume 23-35. Cyanamid code

			PA-440-005. BASF code V186. Non-GLP. Unpublished. **This report is a revised version of report PA-440-004.**
PA-244-017	Khunachak A	1987	THIMET phorate (CL 35,024): validation of GC method M-1705 for the determination of total CL 35,024-related residues in potato flakes, chips, and granules. Princeton, NJ, USA: American Cyanamid Company Inc., report C-2867. Cyanamid code PA-244-017. BASF code V050. Non-GLP. Unpublished.
PA-326-017	Khunachak A	1995	CL 35,024: refrigerator and freezer storage stabilities of total CL 35,024-related residues in cow's milk (interim report). Columbia, MO, USA: ABC Laboratories Inc., report RES 95-161. Cyanamid code PA-326-017. BASF code V117. GLP. Unpublished. **Extended storage stability is found in Khunachak, 1998, PA-705-007.**
PA-705-007	Khunachak A	1998	CL 35,024: refrigerator and freezer storage stabilities of total CL 35,024-related residues in cow's milk. Columbia, MO, USA: ABC Laboratories Inc., report RES 95-161.01, ABC report 426851. Cyanamid code PA-705-007. BASF code V393. GLP. Unpublished.
PA-245-003	Khunachak A and Witkonton S	1995	Phorate (CL 35,024): independent laboratory validation of method M-2461 for the determination of total CL 35,024-related residues in cattle muscle, liver, kidney, and fat and method M-2469 for the determination of total CL 35,024-related residues in cow's milk. USA: ABC Laboratories Inc., report RES 95-150. Cyanamid code PA-245-003. BASF code V079. GLP. Unpublished.
PA-724-017	Kleiner A	1990	CL 35,024 (Phorate/20CR): residues of CL 35,024 in potatoes (AT HILLING; WI, 1988). Princeton, NJ, USA: American Cyanamid Company Inc., report C-3312. Cyanamid code PA-724-017. BASF code V461. GLP. Unpublished.
PA-724-018	Kleiner A	1990	CL 35,024 (Phorate/20CR): residues of CL 35,024 in potatoes (AT HILLING; ID, 1988). Princeton, NJ, USA: American Cyanamid Company Inc., report C-3311. Cyanamid code PA-724-018. BASF code V462. GLP. Unpublished.
PA-620-002	Lavin M	1987	Aerobic soil metabolism of ^{14}C-phorate. Columbia, MO, USA: ABC Laboratories Inc., report #33733. Cyanamid code PA-620-002. BASF code V349. Non-GLP. Unpublished.
PA-720-008	Leonard R	1991	CL 35,024 (Phorate/20G): residues of total CL 35,024-related residues in dry beans after application at the maximum labelled use rate (at planting; CO; 1990). Princeton, NJ, USA: American Cyanamid Company Inc., report C-3575. Cyanamid code PA-720-008. BASF code V405. GLP. Unpublished.
PA-720-010	Leonard R	1991	CL 35,024 (Phorate/20G): residues of total CL 35,024-related residues in dry beans after application at the maximum labelled use rate (at planting; CA; 1990). Princeton, NJ, USA: American Cyanamid Company Inc., report C-3574. Cyanamid code PA-720-010. BASF code V407. GLP. Unpublished.
PA-720-011	Leonard R	1991	CL 35,024 (Phorate/20G): residues of total CL 35,024-related residues in dry beans after application at the maximum labelled use rate (at planting; ID; 1990). Princeton, NJ, USA: American Cyanamid Company Inc., report C-3576. Cyanamid code PA-720-011. BASF code V408. GLP. Unpublished.
PA-720-012	Leonard R	1991	CL 35,024 (Phorate/20G): residues of total CL 35,024-related residues in dry beans after application at the maximum labelled use rate (at planting; NE; 1990). Princeton, NJ, USA: American Cyanamid Company Inc., report C-3580. Cyanamid code PA-720-012. BASF code V409. GLP. Unpublished.
PA-720-013	Leonard R	1991	CL 35,024 (Phorate/20G): residues of total CL 35,024-related residues in dry beans after application at the maximum labelled use rate (at planting; ND; 1990). Princeton, NJ, USA: American Cyanamid Company Inc., report C-3579. Cyanamid code PA-720-013. BASF code V410. GLP. Unpublished.
PA-720-014	Leonard R	1991	CL 35,024 (Phorate/20G): residues of total CL 35,024-related residues in dry beans after application at the maximum labelled use rate (at planting; MN; 1990). Princeton, NJ, USA: American Cyanamid Company Inc., report C-3578. Cyanamid code PA-720-014. BASF code V411. GLP. Unpublished.
PA-720-015	Leonard R	1991	CL 35,024 (Phorate/20G): residues of total CL 35,024-related residues in dry beans after application at the maximum labelled use rate (at planting; MI; 1990). Princeton, NJ, USA: American Cyanamid Company Inc., report C-3577. Cyanamid code PA-720-015. BASF code V412. GLP. Unpublished.
PA-724-013	Leonard R	1991	Effects of cooking on CL 35,024-related residues in potatoes (5X labelled use rate administered at planting; ND; 1990). American Cyanamid Company Inc., report C-3520. Cyanamid code PA-724-013. BASF code V457. GLP. Unpublished.
PA-730-027	Leonard R	1991	CL 35,024 (phorate/20G): residues of CL 35,024-related residues in field corn after application at 5X the labelled use rate (at planting / at cultivation; NE; 1990). Princeton, NJ, USA: American Cyanamid Company Inc., report C-3518. Cyanamid code PA-730-027. BASF code V515. GLP. Unpublished.
PA-730-029	Leonard R	1991	CL 35,024 (phorate/20G): residues of CL 35,024-related residues in field corn after application at 5X the labelled use rate (at planting / at cultivation; IA;

			1990). Princeton, NJ, USA: American Cyanamid Company Inc., report C-3519. Cyanamid code PA-730-029. BASF code V517. GLP. Unpublished.
PA-730-028	Leonard R	1991	CL 35,024 (phorate/20G): residues of CL 35,024-related residues in grain sorghum after application at 5X the labelled use rate (at planting / at cultivation; KS; 1990). Princeton, NJ, USA: American Cyanamid Company Inc., report C-3522. Cyanamid code PA-730-028. BASF code V516. GLP. Unpublished.
PA-730-026	Leonard R	1991	CL 35,024 (phorate/20G): residues of CL 35,024-related residues in grain sorghum after application at 5X the labelled use rate (at planting / at cultivation; TX; 1990). Princeton, NJ, USA: American Cyanamid Company Inc., report C-3523. Cyanamid code PA-730-026. BASF code V514. GLP. Unpublished.
PA-720-010	Leonard R	1992	CL 35,024 (Phorate/20G): residues of total CL 35,024-related residues in dry beans after application at the maximum labelled use rate (at planting; CA; 1990). Report Amendment #1. Princeton, NJ, USA: American Cyanamid Company Inc., report C-3574.1. Cyanamid code PA-720-010. BASF code V407. GLP. Unpublished. **Amendment on Leonard 1991, PA-720-010.**
PA-724-009	Leonard R	1992	CL 35,024 (phorate): effect of cooking on the residues of total CL 35,024-related compounds in potatoes treated with a 5X application of THIMET 20G soil and systemic insecticide (17.3 oz a.i./1000 ft row or 15.7 lbs a.i./A; Idaho - 1991). Princeton, NJ, USA: American Cyanamid Company Inc., report C-3896. Cyanamid code PA-724-009. BASF code V453. GLP. Unpublished.
PA-724-008	Leonard R	1992	CL 35,024 (phorate): effects of processing potatoes into wet and dry peels, granules and chips and microwaving potatoes on the residues of total CL 35,024-related compounds; potatoes treated with a 5X application of THIMET 20G soil and systemic insecticide (17.3 oz a.i./1000 foot row or 14.9 lbs a.i./A; North Dakota -1991). Princeton, NJ, USA: American Cyanamid Company Inc., report C-3895. Cyanamid code PA-724-008. BASF code V452. GLP. Unpublished.
PA-720-003	Leonard R	1994	THIMET 20G: Total CL 35,024-related residues in snap beans after a single banded or side-dressed application of THIMET 20G soil and systemic insecticide made at planting (OR; 1993). Report amendment #1. Princeton, NJ, USA: American Cyanamid Company, report RES 94-060.01. Cyanamid code PA-720-003. BASF code V400. GLP. Unpublished.
PA-720-004	Leonard R	1994	THIMET 20G: Total CL 35,024-related residues in snap beans after a single banded or side-dressed application of THIMET 20G soil and systemic insecticide made at planting (NY; 1993). Report amendment #1. Princeton, NJ, USA: American Cyanamid Company, report RES 94-061.01. Cyanamid code PA-720-004. BASF code V401. GLP. Unpublished.
PA-720-005	Leonard R	1994	THIMET 20G: Total CL 35,024-related residues in snap beans after a single banded or side-dressed application of THIMET 20G soil and systemic insecticide made at planting (MI; 1993). Report amendment #1. Princeton, NJ, USA: American Cyanamid Company, Report RES 94-062.01. Cyanamid code PA-720-005. BASF code V402. GLP. Unpublished.
PA-720-006	Leonard R	1994	THIMET 20G: Total CL 35,024-related residues in snap beans after a single banded or side-dressed application of THIMET 20G soil and systemic insecticide made at planting (WI; 1993). Report amendment #1. Princeton, NJ, USA: American Cyanamid Company Inc, report RES 94-063.01. Cyanamid code PA-720-006. BASF code V403. GLP. Unpublished.
PA-720-007	Leonard R	1994	THIMET 20G: Total CL 35,024-related residues in snap beans after a single banded or side-dressed application of THIMET 20G soil and systemic insecticide made at planting (FL 1993). Princeton, NJ, USA: American Cyanamid Company Inc., report RES 94-064. Cyanamid code PA-720-007. BASF code V404. GLP. Unpublished.
PA-730-022	Leonard R	1994	THIMET 20G: residues of total CL 35,024 related residues in grain sorghum after 5X applications of THIMET 20G soil and systemic insecticide at planting and at cultivation (NE; 1993). Princeton, NJ, USA: American Cyanamid Company Inc., report RES 94-056. Cyanamid code PA-730-022. BASF code V510. GLP. Unpublished.
PA-730-023	Leonard R	1994	THIMET 20G: residues of total CL 35,024 related residues in grain sorghum after 5X applications of THIMET 20G soil and systemic insecticide at planting and at cultivation (TX; 1993). Princeton, NJ, USA: American Cyanamid Company Inc., report RES 94-057. Cyanamid code PA-730-023. BASF code V511. GLP. Unpublished.
PA-730-024	Leonard R	1994	THIMET 20G: residues of total CL 35,024 related residues in grain sorghum after 5X applications of THIMET 20G soil and systemic insecticide at planting and at cultivation (MO; 1993). Princeton, NJ, USA: American Cyanamid

			Company Inc., report RES 94-058. Cyanamid code PA-730-024. BASF code V512. GLP. Unpublished.
PA-730-025	Leonard R	1994	THIMET 20G: residues of total CL 35,024 related residues in grain sorghum after 5X applications of THIMET 20G soil and systemic insecticide at planting and at cultivation (KS; 1993). Princeton, NJ, USA: American Cyanamid Company Inc. report RES 94-059. Cyanamid code PA-730-025. BASF code V513. GLP. Unpublished.
PA-730-068	Leonard R	1995	THIMET 20G: total apparent CL 35,024-related residues in field corn grain after sequential at planting and at cultivation 10X maximum labelled use rate banded applications of Thimet 20G soil and systemic insecticide at 60 oz. formulated product per 1000 foot row per application (IA, 1994). Princeton, NJ, USA: American Cyanamid Company Inc., report RES 95-073. Cyanamid code PA-730-068. BASF code V556. GLP. Unpublished.
PA-705-006	Leonard R	1995	Phorate (CL 35,024): Magnitude of CL 35,024 and its cholinesterase inhibiting metabolites in milk and edible tissues (muscle, liver, kidney and fat) from dairy cattle after oral administration of phorate for 28 consecutive days. Princeton, NJ, USA: American Cyanamid Company Inc., report RES 95-143. Columbia, MO, USA: ABC Laboratories, report no 42634. Cyanamid code PA-705-006. BASF code V392. GLP. Unpublished.
PA-705-008	Leonard R	1995	Addendum to phorate (CL 35,024): Magnitude of CL 35,024 and its cholinesterase inhibiting metabolites in milk and edible tissues (muscle, liver, kidney and fat) from dairy cattle after oral administration of phorate for 28 consecutive days. Princeton, NJ, USA: American Cyanamid Company Inc., report RES 95-143. Columbia, MO, USA: ABC Laboratories, report no 42634. Cyanamid code PA-705-008. BASF code V394. GLP. Unpublished.
PA-140-002	Luckhowec JJ	1989	Pesticide assessment and guideline subdivision D: product chemistry requirements for the technical grade active ingredient (TGAI) and manufacturing use product (MP) THIMET phorate: section 63-2 to 63-21, physical and chemical characteristics. Princeton, NJ, USA: American Cyanamid Company, laboratory report CHDV, Vol. 29, No.12. Cyanamid code PA-140-002, BASF code V007. Non-GLP. Unpublished.
PA-790-013	Manuel A and Whitney K	1976	THIMET 5-G: determination of total THIMET (O,O-diethyl-S-[(ethylthio)methyl]phosphorodithioate)-related residues in coffee beans. (Colombia, South America, 1975). Princeton NJ, USA: American Cyanamid Company Inc., report C-963. Cyanamid code PA-790-013, BASF code V608. Non-GLP. Unpublished.
PA-630-005	Martin C and Heim D	1999	^{14}C-Phorate (AC 35,024) and its sulfoxide (CL 18,177) and sulfone (CL 18,161) metabolites: hydrolysis in sterile pH 5, 7, and 9 buffers. Princeton, NJ, USA: American Cyanamid Company, project no. ENV 97-019. Cyanamid code PA-630-005. BASF code V371. GLP. Unpublished.
PA-905-047	Metcalf RL, Fukuto TR, March RB	1957	Plant metabolism of dithio-systox and thimet. USA: University of California. Journal of Economic Entomology, 50(3): 338-345. Cyanamid code PA-905-047. BASF code V686. Non-GLP. Published.
PA-440-008	Miller P	1986	Thimet insecticide, phorate (CL 35,024): metabolite identification in goat's milk and tissues. A summary. Princeton, NJ, USA, American Cyanamid Company, no report number. Cyanamid code PA-440-008. BASF code V189. Non-GLP. Unpublished. **This report is a summary of report PA-440-003 and PA-440-005, contains no new information.**
PA-440-006	Miller P	1991	Phorate (CL 35,024): metabolic fate of carbon-14 labeled CL 35,024 in tissues and eggs of the laying hen. Princeton, NJ, USA: American Cyanamid Company, report no PD-M 28-39. Cyanamid code PA-440-006. BASF code V187. GLP. Unpublished.
-	PAM	1963-1973	Pesticide Analytical Manual Vol. II Pesticide Reg. Sec. 180.206 Phorate. Method I, A-L. Non-GLP. Published.
PA-730-013	Peterson RP	1973	Residues in field corn, planted in 20-inch rows (grain and forage). USA: Hazleton Laboratories Inc., report C-323. Cyanamid code PA-730-013. BASF code V501. Non-GLP. Unpublished.
PA-790-020	Peterson RP	1981	THIMET phorate (CL 35,024): residues of total CL 35,024-related compounds in green and roasted coffee beans. Princeton, NJ, USA: American Cyanamid Company Inc., report C-1938. Cyanamid code PA-790-020. BASF code V501. Non-GLP. Unpublished.
PA-244-025	Peterson RP	1987	THIMET phorate (CL 35,024): validation of GC method M-1683 for the determination of total CL 35,024-related residues in sugar beet roots and tops. Princeton, NJ, USA: American Cyanamid Company Inc., report C-2847. Cyanamid code PA-244-025. BASF code V058. Non-GLP. Unpublished.
PA-326-011	Peterson RP	1987	THIMET Phorate (CL 35,024): freezer stability of total CL 35,024-related residues in sugar beet roots and tops. Princeton, NJ, USA: American Cyanamid

			Company Inc., report C-2917. Cyanamid code PA-326-011. BASF code V111. Non-GLP. Unpublished. **Extended storage stability is found in Peterson, 1987, PA-326-009.**
PA-326-009	Peterson RP	1987	THIMET insecticide phorate (CL 35,024): freezer stability of total CL 35,024-related residues in sugar beet roots and tops. Princeton, NJ, USA: American Cyanamid Company Inc., report C-3000. Cyanamid code PA-326-009. BASF code V109. Non-GLP. Unpublished.
PA-724-024	Peterson RP	1987	THIMET Phorate (CL 35,024/20-G): residues of total CL 35,024-related compounds in sugar beet tops and roots (BAND, DRILL, FOL; ID, 1985). USA: Analytical Bio-Chemistry Laboratories, report C-2907. Cyanamid code PA-724-024. BASF code V468. Non-GLP. Unpublished.
PA-730-042	Potts CR	1986	THIMET phorate (CL 35,024/20-G): residues of total CL 35,024-related compounds in corn grain, oil and meal (BAND, CULT, FOL; IL, 1985). Princeton, NJ, USA: American Cyanamid Company Inc., report C-2804. Cyanamid code PA-730-042. BASF code V530. Non-GLP. Unpublished.
PA-326-010	Potts CR	1987	THIMET phorate (CL 35,024): freezer stability of total CL 35,024-related residues in refined corn oil and corn meal. Princeton, NJ, USA: American Cyanamid Company Inc., report C-2908. Cyanamid code PA-326-010. BASF code V110. Non-GLP. Unpublished. **This report is replaced by Potts, 1987, PA-326-006.**
PA-326-006	Potts CR	1987	THIMET phorate (CL 35,024): freezer stability of total CL 35,024-related residues in refined corn oil and corn meal. Princeton, NJ, USA: American Cyanamid Company Inc., report C-2908.1. Cyanamid code PA-326-006. BASF code V106. Non-GLP. Unpublished. **Extended storage stability is found in Potts, 1987, PA-326-008.**
PA-326-008	Potts CR	1987	THIMET phorate (CL 35,024): freezer stability of total CL 35,024-related residues in refined corn oil and corn meal. Princeton, NJ, USA: American Cyanamid Company Inc., report C-2996. Cyanamid code PA-326-008. BASF code V108. Non-GLP. Unpublished.
PA-730-041	Potts CR	1987	THIMET phorate (CL 35,024/20-G): residues of total CL 35,024-related compounds in corn grits, flour, hulls and presscake (BAND, CULT, FOL; IL, 1985). Princeton, NJ, USA: American Cyanamid Company Inc., report C-2865. Cyanamid code PA-730-041. BASF code V529. Non-GLP. Unpublished.
PA-730-039	Potts CR	1987	THIMET phorate (CL 35,024/20-G): residues of total CL 35,024-related compounds in corn germ (BAND, CULT, FOL; IL, 1985). Princeton, NJ, USA: American Cyanamid Company Inc., report C-2904. Cyanamid code PA-730-039. BASF code V527. Non-GLP. Unpublished.
PA-730-034	Potts CR	1987	THIMET phorate (CL 35,024/20-G): residues of total CL 35,024-related compounds in corn soapstock and a summary of residues in all corn processed commodities (BAND, CULT, FOL; IL, 1985). Princeton, NJ, USA: American Cyanamid Company Inc., report C-2937. Cyanamid code PA-730-034. BASF code V522. Non-GLP. Unpublished.
PA-731-006	Roman M	1982	THIMET phorate (CL 35,024/15-G): residues of total CL 35,024-related compounds in sorghum fodder and grain (BOTR; CO, 1981). Princeton, NJ, USA: American Cyanamid Company Inc., report C-1982. Cyanamid code PA-731-006. BASF code V572. Non-GLP. Unpublished.
PA-244-032	Roman M	1985	THIMET phorate (CL 35,024): validation of GC method M-1599 for the determination of total CL 35,024-related residues in corn grain. Princeton, NJ, USA: American Cyanamid Company Inc., report C-2657. Cyanamid code PA-244-032. BASF code V065. Non-GLP. Unpublished.
PA-730-059	Roman M	1986	THIMET (phorate, CL 35,024/20-G): residues of total CL 35,024-related compounds in corn grain (BAND, CULT; IL, 1985). USA: American Cyanamid Company Inc. report C-2699. Cyanamid code PA-730-059. BASF code V547. Non-GLP. Unpublished.
PA-730-061	Roman M	1986	THIMET (phorate, CL 35,024/20-G): residues of total CL 35,024-related compounds in corn grain (BAND, FOL; IL, 1985). USA: American Cyanamid Company Inc. report C-2701. Cyanamid code PA-730-061. BASF code V549. Non-GLP. Unpublished.
PA-730-062	Roman M	1986	THIMET (phorate, CL 35,024/20-G): residues of total CL 35,024-related compounds in corn grain (BAND, CULT, FOL; IL, 1985). USA: American Cyanamid Company Inc., report C-2702. Cyanamid code PA-730-062. BASF code V550. Non-GLP. Unpublished.
PA-326-015	Roman M	1987	THIMET phorate (CL 35,024): freezer stability of total CL 35,024-related residues in corn commodities: green plants, straw and grain. Princeton, NJ, USA: American Cyanamid Company Inc., report. C-2880. Cyanamid code PA-326-015. BASF code V115. Non-GLP. Unpublished. **Extended storage stability is found in Roman, 1987, PA-326-007 and Roman, 1988, PA-326-**

			003.
PA-326-007	Roman M	1987	THIMET phorate (CL 35,024): freezer stability of total CL 35,024-related residues in corn commodity: green plants, straw and grain. Princeton, NJ, USA: American Cyanamid Company Inc., report C-2989. Cyanamid code PA-326-007. BASF code V107. Non-GLP. Unpublished. **Extended storage stability is found in Roman, 1988, PA-326-003.**
PA-730-067	Roman M	1987	THIMET Phorate (CL 35,024/20-G): residues of CL 35,024 and its five potential metabolites in green corn plants and corn straw (BAND, CULT, FOL; FL, WI, NB, OR). Princeton, NJ, USA: American Cyanamid Company Inc., report C-2869. Cyanamid code PA-730-067. BASF code V555. Non-GLP. Unpublished.
PA-326-003	Roman M	1988	CL 35,024 (phorate): freezer stability of total CL 35,024-related residues in corn commodities: green plants, straw and grain (final report). Princeton, NJ, USA: American Cyanamid Company Inc., report C-3102. Cyanamid code PA-326-003. BASF code V103. Non-GLP. Unpublished.
PA-905-049	Schulz KR, Fuhremann TW and Lichtenstein EP	(1976)	Interaction of pesticide chemicals. Effect of Eptam and its antidote on the uptake and metabolism of ^{14}C phorate in corn plants. J. Agric. Food Chem. Vol. 24 No. 2, 296-299. Cyanamid code PA-905-049. BASF code V688. Non-GLP. Published.
PA-724-022	Shimel KT	1987	THIMET Phorate (CL 35,024/20-G): residues of total CL 35,024-related compounds in processed potato flakes, chips, granules, and potato tubers (IF; ID, 1985). Princeton, NJ, USA: American Cyanamid Company Inc., report C-2923. Cyanamid code PA-724-022. BASF code V466. Non-GLP. Unpublished.
PA-750-004	Snyder E and Gillespie J	1975	THIMET 600: total THIMET-related residues in cottonseed following aerial application of THIMET 600 (Arizona). Princeton, NJ, USA: American Cyanamid Company Inc., report C-856. Cyanamid code PA-750-004. BASF code V590. Non-GLP. Unpublished.
PA-905-052	Sonobe H, Carver RA, Krause RT and Kamps LR	1982	Extraction of biologically incorporated ^{14}C-phorate residues from root crops. Tokyo, Japan:. J. Agric. Food Chem. 30:696-702. Cyanamid code PA-905-052. BASF code V691. Non-GLP. Published.
-	Tomlin CDS (editor)	2000	The pesticide manual - A world compendium. 12th ed. UK, British Crop Protection Council. Non-GLP. Published.
PA-905-048	Zaki MM and El-Sayed MM	1968	Translocation and metabolism of certain systemics topically applied to cotton plants. Egypt: Ain Shams University. Bull. ent. Soc. Egypt Econ. Ser. II, pp 112-120. Cyanamid code PA-905-048. BASF code V687. Non-GLP. Published.